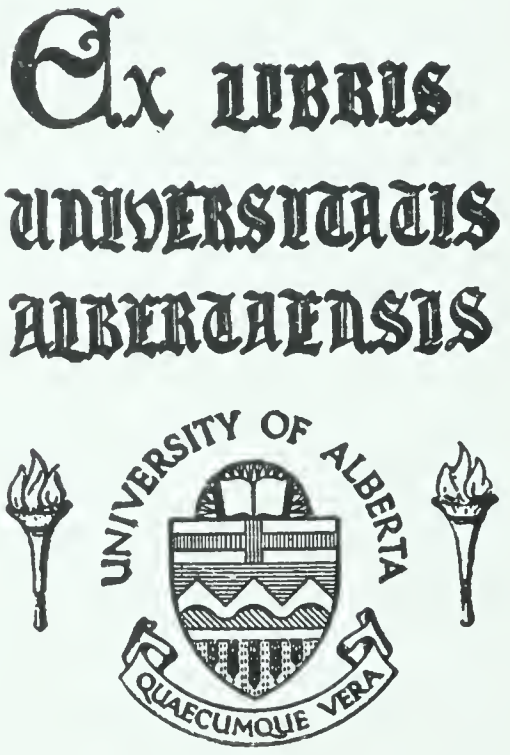
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RADIOLYSIS OF CYCLOPENTANONE

by

DAVID L. DUGLE

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

SEPTEMBER, 1964

UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled RADIOLYSIS OF CYCLOPENTANONE submitted by DAVID L. DUGLE in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

ABSTRACT

The initial G values of the major products arising from the Co^{60} γ radiolysis of pure cyclopentanone are: hydrogen (0.75), carbon monoxide (0.68), ethylene (0.80), cyclopentanol (0.84), 4-pentenal (0.84), total dimer (1.0) and polymer (excluding dimer) (1.9 cyclopentanone units). Yields of a number of minor ($G < 0.1$) products were also determined. These products were methane, ethane, acetylene, propylene, n-butane, 1-butene, cyclobutane, methylcyclopropane and cyclopentenone.

The radiolytic yields of hydrogen, cyclopentanol, and the dimers are reduced when benzene is added to cyclopentanone prior to radiolysis. Added benzene sensitizes the formation of ethylene, carbon monoxide, 4-pentenal and some of the minor products. These inhibition and sensitization effects are probably due to activation transfer processes. The inhibition of the hydrogen yields from cyclopentanone-benzene solutions is independent of the dose rate.

In addition to causing a greater amount of inhibition of the formation of hydrogen, cyclopentanol, and the dimers than did benzene; 1,3-pentadiene also reduced the yields of all of the other major products.

The effects of oxygen, benzene, and 1,3-pentadiene on the yield of 4-pentenal are most readily explained by postulating that about 70% of the aldehyde is produced from the lowest triplet level of a cyclopentanone molecule.

The formation of products arising from C-C bond cleavage and the effects of additives on their yields can be explained in terms of a biradical mechanism.

The effects of additives on the yields of products arising from C-H bond cleavage can be accounted for by their relative radical scavenging abilities.

The radiolytic behavior of cyclopentanone is very similar to that of cyclohexanone.

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I. INTRODUCTION

Radiation chemistry is the study of the chemical effects produced in a system by the absorption of ionizing radiation. The radiation may consist of either particles (α- or β-rays) or electromagnetic radiation (γ-rays) which are emitted by the decay of naturally occurring unstable isotopes. It might also consist of accelerated particles (e.g. protons or deuterons) or artificial electromagnetic radiation (x-rays) (Friedlander and Kennedy, 1949).

The present study was carried out with Co^{60} γ-rays. Naturally occurring cobalt (Co^{59}) is converted to Co^{60} through the absorption of a neutron by irradiation in a pile. The Co^{60} isotope, which has a half-life of 5.25 years, emits a 0.31 MeV β-particle and is thereby transformed into an isotope of nickel (Ni^{60}) which has an excited nucleus. In the process of losing this excitation energy, two gamma rays are emitted which have energies of 1.17 and 1.33 MeV respectively. Since these gamma rays have almost equal energies and are emitted in equal numbers, and since the 0.31 MeV β-rays have a range of less than 0.5 mm in glass (Cowan, 1956), the chemical effects caused by the Co^{60} isotope may be considered to be due to the absorption of monoenergetic (1.25 MeV) gamma rays.

The interaction of photons of this energy with matter will be considered in the following section.

A. Interaction of Electromagnetic Radiation with Matter

There are three processes by which photons of the energies commonly used in radiation chemistry may react with matter. These are the photoelectric process, the Compton process, and the pair-production process (Johns and Laughlin, 1956). The total mass absorption coefficient (μ/ρ) for these three processes is given by expression I-1.

$$\mu/\rho = \sigma_a/\rho + \tau/\rho + \kappa/\rho \qquad \text{(I-1)}$$

where σ_a/ρ is the true Compton mass absorption coefficient, κ/ρ is the pair-production mass absorption coefficient, τ/ρ is the photoelectric mass absorption coefficient and ρ is the density of the medium. For a low atomic number absorber (e.g. water or a ketone) energy absorption from photons possessing energies of about 1 MeV (e.g. Co^{60} γ-rays) is predominantly due to the Compton process since the absorption coefficients of the other two processes are negligible, as shown in Fig. I 1. Therefore only the Compton process will be discussed.

The Compton effect involves an interaction between a photon which is traversing a medium and a free or a bound electron in the medium. This interaction causes energy to be transferred from the photon to the electron.

FIGURE I 1

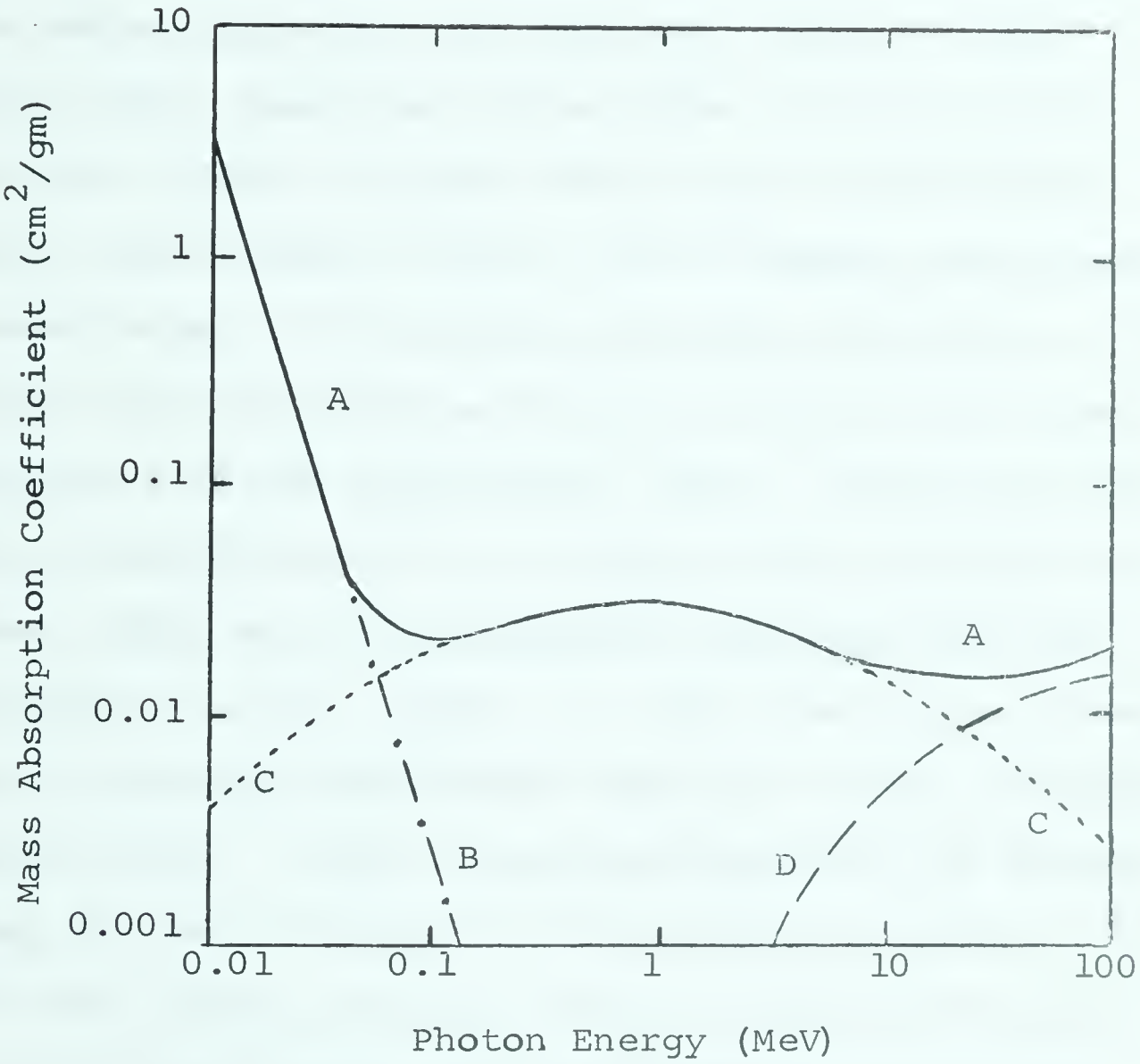
Absorption of Photon Energy by Water.

A = μ/ρ = total mass absorption coefficient.

B = τ/ρ = photoelectric mass absorption coefficient.

C = σ_a/ρ = true Compton mass absorption coefficient.

D = κ/ρ = pair-production mass absorption coefficient.


10
1
0.1
0.01
0.001
0.01
0.1
1
10
100
Mass Absorption Coefficient (cm²/gm)
Photon Energy (MeV)
A
A
B
C
C
D

A lower energy photon (scattered photon) is produced together with an accelerated electron (primary electron). The scattered photon may undergo further 'collisions' resulting in the loss of a portion of its remaining energy or it may be completely absorbed by an atom in the medium (photoelectric effect). Since a 1 MeV photon has a mean free path of about 33 cm in water (Andrews, 1961) it is not likely that the scattered photon would react in the 2 - 10 ml samples used in the present study. The primary electrons produced by a 1 MeV photon may have energies of up to 0.8 MeV with a mean value of 0.45 MeV (Kuppermann, 1959). Since the range of a 1 MeV β-particle is 4.1 mm in water (Spinks and Woods, 1964) most of the primary electrons would be absorbed in a 2 ml sample. A 1 MeV electron may undergo several thousand collisions before its energy is dissipated (Johns, 1961). Ions and excited molecules are formed along the path ('track') of the primary electrons. A 0.45 MeV primary electron travels an average distance of about 4500 Å along the track between ionizations (Charlesby, 1960). The electrons produced by ionizations caused by the primary electrons are called secondary electrons. The secondary electrons may possess sufficient energy to cause further ionization as well as excitations. Since the number of ion pairs produced by a charged

particle per unit volume (ion density) increases rapidly with decreasing energy, the bulk of the ionizations is confined to a rather short distance from the site of production of the secondary electron (~10-15 Å) (Burton, 1959). The spatial distribution of the ionization produced by a secondary electron is called a 'spur' (Burton et al., 1958).

Since the Compton absorption coefficient per atom is proportional to the atomic number, z, the relative amount of absorption by different compounds is proportional to their electron densities.

A proposed time scale for the events following the absorption of energy by the system and leading up to product formation will be considered in the next section.

B. Duration of Events Following the Absorption of Energy by the System

The approximate time scale for events following the absorption of energy by a system has been divided into three stages by Platzmann (1958) and Kuppermann (1959).

1. Physical Stage

The ionized and excited species which are responsible for the products formed as a result of the irradiation of a given system are produced in a time interval of about 10^{-15} sec. The absorption of energy by the system is therefore essentially completed before chemical changes begin to occur.

2. Physicochemical Stage

This stage has a duration of about 10^{-12} sec which is of the same order of magnitude as a molecular vibration time. During this stage the excited molecules and ions formed in the physical stage reach thermal equilibrium. Ion molecule reactions, dissociations of excited molecules in repulsive states, and energy transfer reactions occur.

3. Chemical Stage

The chemically reactive species produced in the physicochemical stage undergo reaction. Radical-radical reactions occur in the spurs during the early part of this stage. As time proceeds the remaining radicals diffuse into the bulk of the medium where they may react with available solutes.

A consideration of the reactions of the radicals, ions and excited molecules produced by the absorption of ionizing radiation by a system will be given in the next section.

C. The Reactions of Excited Molecules and Ionic Species

1. Ions

The rather high dielectric constant of cyclopentanone ($\sim$14[1]) may lead to a significant contribution by ions to

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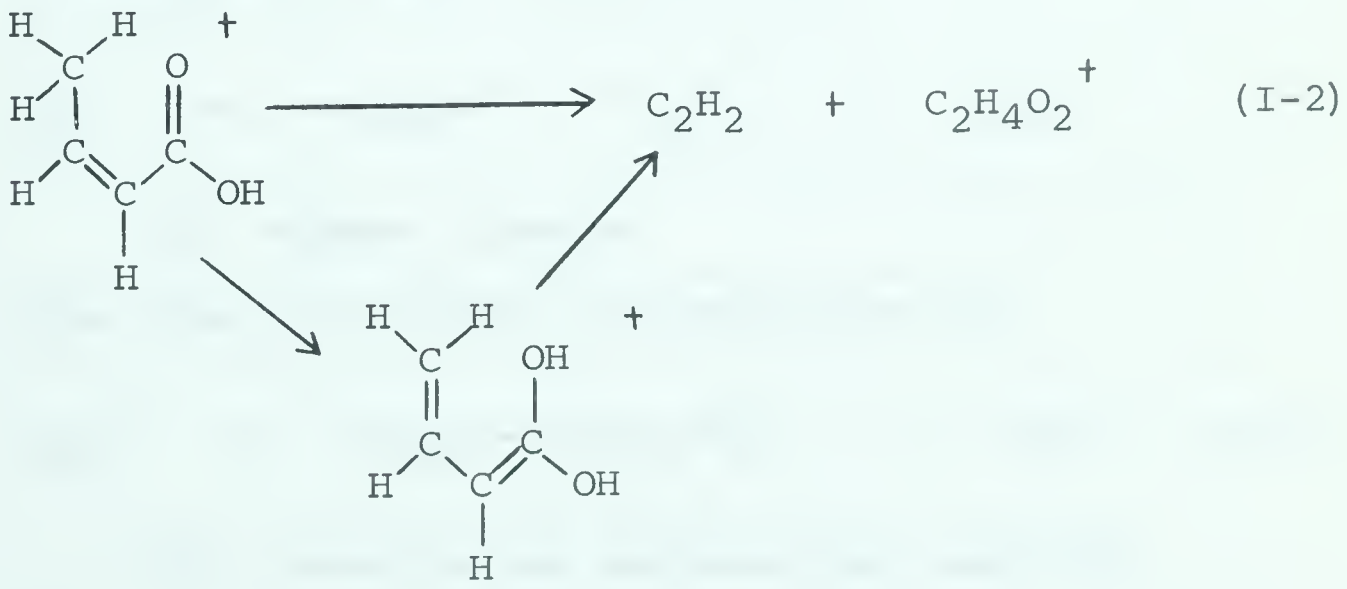
1. Various values have been reported for the dielectric constant of liquid cyclopentanone: 16.3 (-51°C), White and Bishop, 1940; 13.45 (20°C), Timmermanns et al., 1955; 13.56 (25°C), Gäumann et al., 1956; $\sim$20 (?), Lange, 1961.

the formation of the products from radiolyzed liquid phase cyclopentanone. Since very little evidence has been obtained which demonstrates the occurrence of ion-molecule reactions or of unimolecular rearrangements or dissociations involving the ionic intermediates in the liquid phase, it is often necessary to consider data obtained from mass spectrometric studies of vapors at low pressure. An example of several of the types of reactions which have been investigated is presented below. The importance of negative ion reactions is not known and therefore will not be considered.

a. Unimolecular Rearrangements and Dissociations of Ions

(1) Rearrangements

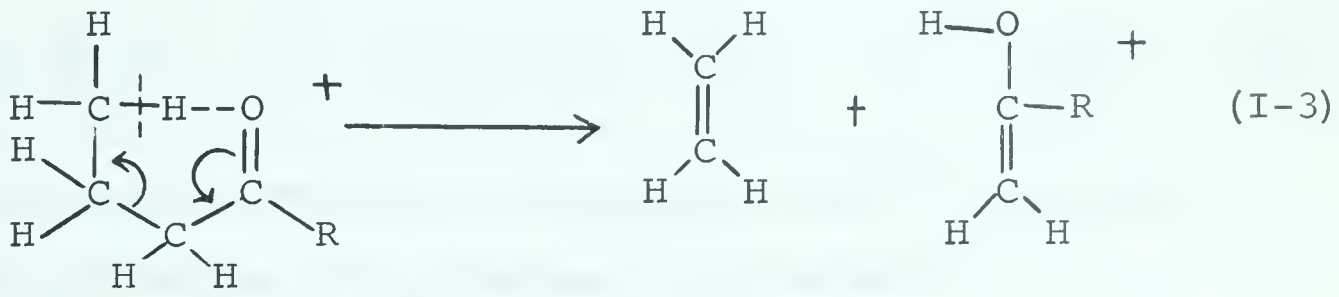
The following rearrangement was proposed by Happ and Stewart (1952) to explain the mass spectral data obtained from isocrotonic acid.



(I-2)

(2) Dissociations

McLafferty (1959) devised a mechanism to explain the decomposition of some aliphatic ketones by electron impact which utilizes a cyclic transition state.



(I-3)

b. Ion Molecule Reactions

(1) Hydride ion transfer

Futrell (1959) has postulated that hydride ion transfer is a key process in the radiolysis of liquid or vapor phase n-hexane.

$$R^+ + C_6H_{14} \longrightarrow RH + C_6H_{13}^+ \qquad \text{(I-4)}$$

(2) Hydrogen atom transfer

An example of such a reaction is:

$$CD_4^+ + C_3H_8 \longrightarrow CD_4H^+ + C_3H_7\cdot \qquad \text{(I-5)}$$

(3) Proton transfer

This type of reaction is exemplified by:

$$C_2H_3^+ + C_2H_4 \longrightarrow C_2H_5^+ + C_2H_2 \qquad \text{(I-6)}$$

(4) Insertion or condensation reactions

An example is:

$$C_6H_6 + CH_3^+ \longrightarrow C_7H_7^+ + H_2 \qquad \text{(I-7)}$$

(5) Electron transfer reactions

The reaction

$$C_6H_{12}^+ + C_6H_6 \longrightarrow C_6H_{12} + C_6H_6^+ \qquad \text{(I-8)}$$

has been postulated by Burton et al. (1958) to account for the protection of cyclohexane by benzene.

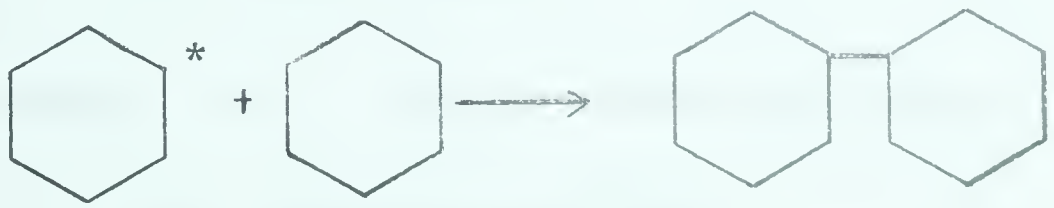
2. Excited Molecules

Excited molecules may be formed during the initial excitation in the track or they may be formed by the neutralization of positive ions by electrons. These methods of formation will probably lead to different products if the ion undergoes reactions with the substrate of the type considered in the previous section before neutralization occurs. Evidence has been reported which indicates that excited molecules may also arise from energy transfer reactions. Cundall et al. (1964) have found that isomerization of 2-butene results from the vapor phase photolysis of the olefin mixed with benzene or pyridine, and that the addition of nitric oxide prior to photolysis resulted in the formation of a crystalline solid which was thought to be $(CH_3CHNO)_2$. Gamma radiolysis of benzene solutions of 2-butene has also been shown to cause isomerization of the olefin (Cundall and Griffiths,

1963). The results obtained from the radiolytic system upon addition of various solutes led Cundall and coworkers to postulate that the isomerization is caused by a triplet state. These authors therefore suggested that energy transfer from a triplet state of the sensitizer (e.g. benzene) to the singlet ground state of the acceptor (e.g. 2-butene) resulted in the formation of a triplet state of the acceptor and the singlet ground state of the sensitizer. Hammond et al. (1962) have reported a similar quenching of the triplet states of carbonyl containing compounds by diolefins.

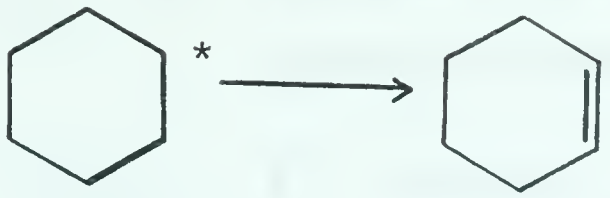
a. Formation of Molecular Products via Bimolecular Reactions

Bimolecular reactions involving an excited molecule have been suggested to explain radiolytic data (Scarborough and Burr, 1962).



b. Formation of Molecular Products by Unimolecular Reactions.

Dyne and Jenkinson (1962) concluded from their data on the isotopic composition of the hydrogen produced by the radiolysis of solutions of c-C_6H_{12} (or c-C_6D_{12}) containing c-C_6D_6 (or c-C_6H_6) that true molecular detachment does occur (equation I-10).

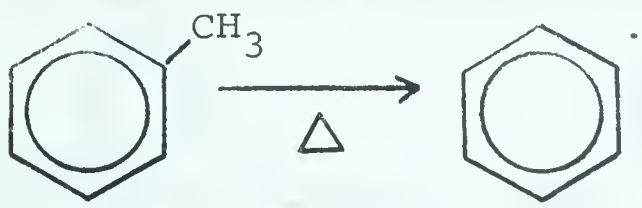


(I-10)

c. Production of Radicals

Radicals may be produced from molecules by absorption of energy from many sources, for example:

$$CH_3COCH_3 + h\nu \longrightarrow CH_3\dot{C}O + \cdot CH_3 \qquad \text{(I-11)}$$



(I-12)



(I-13)

Radicals may undergo a variety of reactions which are exemplified below by the reactions of the cyclohexyl radical.

(1) Combination

$$C_6H_{11}\cdot + C_6H_{11}\cdot \longrightarrow C_6H_{11}\text{-}C_6H_{11} \qquad \text{(I-14)}$$

(2) Disproportionation

$$C_6H_{11}\cdot + C_6H_{11}\cdot \longrightarrow C_6H_{10} + C_6H_{12} \qquad \text{(I-15)}$$

(3) Abstraction of a hydrogen atom (giving rise to a new radical).

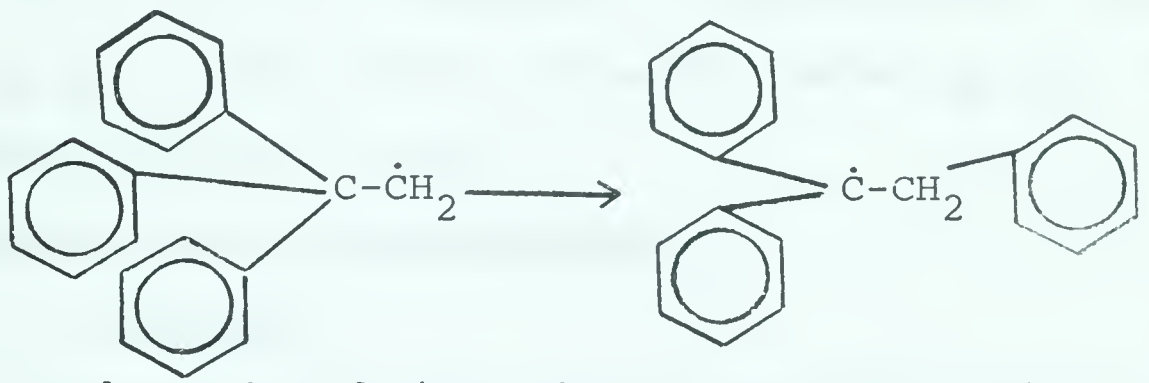
$$C_6H_{11}\cdot + RH \longrightarrow C_6H_{12} + R\cdot \qquad \text{(I-16)}$$

(4) Addition to an olefinic double bond (giving rise to a larger radical).

$$\cdot C_6H_{11} + RCH{=}CHR' \longrightarrow RCH(C_6H_{11})\text{-}\dot{C}HR' \qquad \text{(I-17)}$$

(5) Rearrangement

A more stable radical may be formed by migration of atoms or groups. An example of phenyl migration was reported by Curtin and Hurwitz (1952).



(I-18)

A number of techniques have been used to identify radicals produced in radiolyzed systems. Since molecules containing unpaired electrons are paramagnetic, stable free radicals may be detected by magnetic susceptibility measurements. Lewis et al. (1949) used this technique to determine the presence of unpaired electrons in the phosphorescent (triplet) state of fluorescein. Another technique which depends on the magnetic properties of unpaired electrons is electron spin resonance (ESR). This technique has been reviewed by Ingram (1958) and Dorfman (1961). Ohnishi et al. (1962) have used ESR to identify several free radicals produced by radiolysis at 77°K including phenyl and cyclohexadienyl (from benzene) and

cyclohexyl (from cyclohexane) radicals.

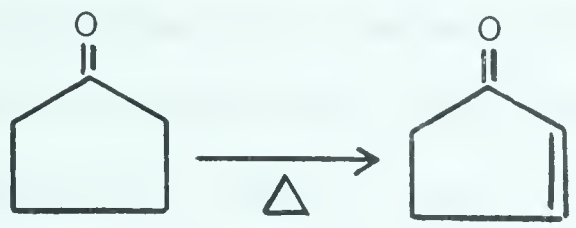
A number of reagents have also been used to detect the presence of free radicals in irradiated organic systems. Holroyd and Klein (1962) added C^{14}-labeled ethylene to several hydrocarbons before irradiation and labeled ethyl radicals were produced by H· atom addition to the olefin. Any products containing C^{14} were then identified and the radical responsible deduced. Other radical scavengers used included: the 1,1'-diphenyl-2-picrylhydrazil radical (Bouby et al., 1961), ferric chloride (Adams et al., 1959), and styrene (Chapiro, 1959).

D. Previous Work on Cyclopentanone

1. Pyrolysis

A comprehensive study of the pyrolysis of cyclopentanone at about 520°C has been reported (Johnson and Walters, 1954). They reported the formation of carbon monoxide, hydrogen, 1-butene, ethylene, propylene, 2-cyclopentenone and lesser quantities of methane, ethane, propane, 1,3-butadiene, and cyclopentadiene. The production of 1,3-butadiene was attributed to the dehydrogenation of 1-butene which is also known to give rise to propylene upon pyrolysis (Wheeler and Wood, 1930). The absence of cyclobutane among the products was attributed by Johnson and Walters (1954) to its pyrolysis (the thermal decomposition of cyclobutane into ethylene has been studied at 425°C [Genaux and Walters, 1951]). Johnson and Walters (1954) did

not look for the isomerization product (4-pentenal) or polymeric material. They suggested that the most important overall reactions are:



$$+ \quad H_2 \qquad \text{(I-19)}$$

$$\xrightarrow[\Delta]{} \quad 1\text{-}C_4H_8 \quad + \quad CO \qquad \text{(I-20)}$$

$$\xrightarrow[\Delta]{} \quad 2\ C_2H_4 \quad + \quad CO \qquad \text{(I-21)}$$

2. Photolysis

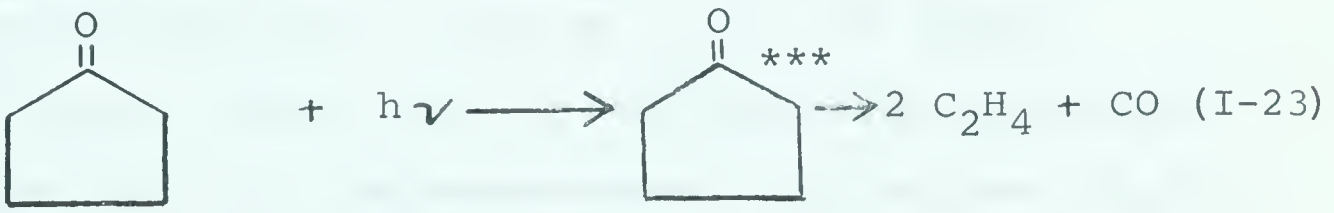
Ethylene, carbon monoxide, 1-butene, and 2-butene were first reported to be the products of the vapor phase photolysis of cyclopentanone (Saltmarsh and Norrish, 1935). It has since been shown that cyclobutane is the only C_4 product and the absence of the butenes among the products was attributed to the strained configuration required for an intramolecular H-atom abstraction reaction (Benson and Kistiakowsky, 1942). These authors also postulated the formation of the tetramethylene acyl biradical to explain their results.

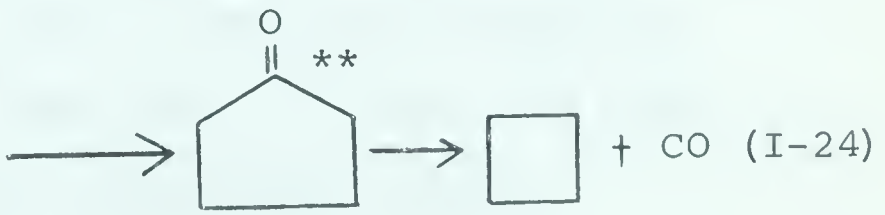
Blacet and Miller (1957) reported that their data from the vapor phase photolysis of cyclopentanone at 3130 A and 125°C obeyed equation I-22, but they found that at higher temperatures and/or shorter wavelengths this relationship no longer held.

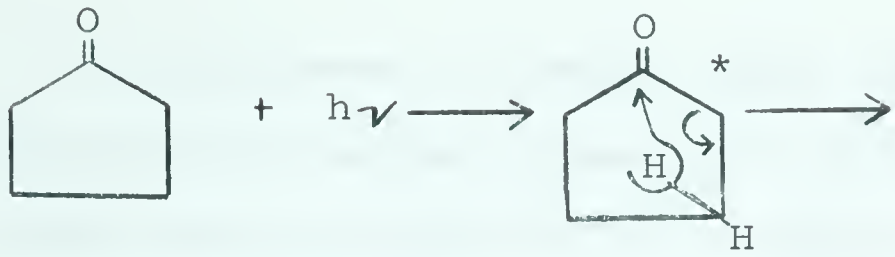
$$\phi_{CO} = \phi_{\text{cyclobutane}} + \tfrac{1}{2}\phi_{C_2H_4} \qquad \text{(I-22)}$$

At shorter wavelengths, however, the yields were found to be independent of temperature. At 2537 Å, for example, the quantum yields were reported to be unchanged over the temperature region from 100 - 300°C. Blacet and Miller (1957) stated that the lack of a temperature dependence at 2537 Å, together with the formation of polymer which they observed, could best be explained in terms of a tetramethylene acyl biradical.

Subsequent studies have failed to show the formation of any polymer, and equation I-22 has been reported to be valid up to 125° at 3130 Å and at higher photon energies up to 300°C (Srinivasan, 1961a). Srinivasan (1959a) first observed the formation of 4-pentenal from both liquid and vapor phase photolysis at 3130 Å, and proposed the following mechanism to explain the formation of the observed products from the photolytic decomposition of cyclopentanone:







(I-25)

where the asterisks are used to indicate varying amounts of vibrational energy in a given excited singlet state of the ketone molecule.

A possible source of the ethylene is an excited cyclobutane molecule as shown in equation I-26.



(I-26)

In order to show that this reaction does not occur, cyclopentanone-2,2,5,5-d_4 was photolyzed and the ethylenes analyzed by mass spectrometry (Srinivasan, 1959a). In other experiments the cyclobutane-1,1,2,2-d_4 obtained from the photolysis of this same ketone was subjected to thermal decomposition at about 450°C (Srinivasan and Kellner, 1959). The labeled ethylenes obtained from the thermal decomposition were formed in the expected statistical ratio of 1:2:1, of CH_2CH_2: CH_2CD_2: CD_2CD_2. Since the only ethylene species produced by the photolysis of cyclopentanone-2,2,5,5-d_4 was CH_2CD_2, the formation of ethylene from an excited cyclobutane molecule was excluded and reactions I-23 and I-24 were concluded to be independent (Srinivasan, 1959a).

Srinivasan and Noyes (1960) reported that the photolysis of acetone mixed with O_2^{18} resulted in the production of acetone-O^{18} in a quantum yield of 0.45. Srinivasan (1961a) has attributed this reaction to a triplet state of the acetone molecule. The photolysis of cyclopentanone in the presence of O_2^{18} was found to give a quantum yield of cyclopentanone-O^{18} of less than 0.03 (Srinivasan, 1961a). This author also failed to observe phosphorescence from a cyclopentanone-solvent glass at 77°K and therefore concluded that if the triplet state of the ketone is involved in photolytic reactions, its lifetime must be less than 10^{-8} seconds. Srinivasan (1961a, 1961b) has also reported that if a foreign gas (e.g. methane, argon, or oxygen) was added to the ketone prior to photolysis, the yield of 4-pentenal increased while that of carbon monoxide decreased. He suggested that these varied effects were not consistent with a biradical mechanism and therefore postulated that reactions I-23, I-24, and I-25 occurred from decreasing vibrational levels in a single excited singlet state and that the reaction which occurred depended upon the amount of vibrational energy in the molecule at the instant of decomposition. Foreign gases were therefore suggested to alter the decompositional path by reducing the vibrational energy. Srinivasan (1961a, 1961b) concluded that

reactions I-23 to I-25 should be considered to be concerted processes until "positive evidence for the diradical mechanism is discovered".

More recently, LaPaglia and Roquitte (1962) have detected the existence of a triplet state of cyclopentanone by observing a phosphorescence maximum at 4400-4500 Å from a ketone-hexane glass at 77°K although no quantum yield for the phosphorescence was given. They estimated that the lifetime of this state is 1.1×10^{-3} seconds.

3. Radiolysis of Cyclopentanone

Studies on the Co^{60} gamma irradiation of pure cyclopentanone and solutions of the ketone containing oxygen, 1,1'-diphenyl-2-picrylhydrazil (DPPH), iodine, cyclohexene, carbon dioxide and ethylene have been reported recently (Katayama and Trumbore, 1964; Bristowe, Katayama and Trumbore, 1964). In order to facilitate comparison among their data and those presented in the present study, the products arising from C-H and C-C bond cleavage will be considered separately. The radiolytic yields of all products will hereafter be expressed in terms of the 'G value' (i.e. the number of molecules produced or destroyed per 100 eV of energy absorbed by the system).

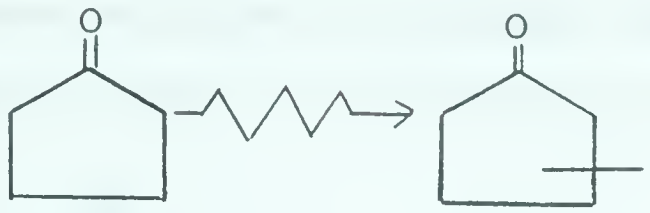
a. Products Arising from C-H Bond Cleavage

(1) Hydrogen

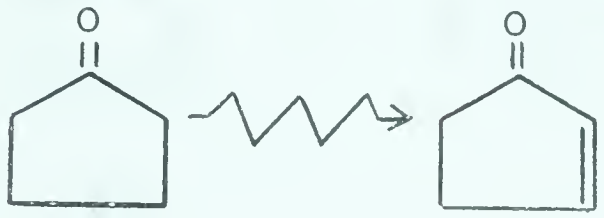
Katayama and Trumbore (1964) found an initial

yield (G value extrapolated to zero dose) for hydrogen of 0.68. The yield was independent of the absorbed dose. They also reported that the hydrogen yield was not affected by: (1) an increase in temperature (25 - 100°C), (2) the vapor to liquid volume ratio in the irradiation cell, or (3) addition of carbon dioxide or ethylene. The effect of slight changes in the surface area of the radiolysis cells on the hydrogen yield was reported to be negligible. These authors found that a 10^{-3}M concentration of iodine, DPPH, or cyclohexene caused a 10-20% reduction of the hydrogen yield, and that DPPH reduced G (hydrogen) more rapidly than iodine. They also irradiated cyclopentanone-2,2,5,5-d_4 and reported that the H_2:D_2 ratio ($\sim$3:1) was independent of dose and temperature (-78° to 25°C), and was not affected by DPPH. A possible source of the unscavengeable HD obtained from two samples of the cyclopentanone-d_4 which contained DPPH or cyclohexene respectively, was proposed to be the molecular elimination of hydrogen from carbons 2 and 3 of an excited ketone molecule (Bristowe et al., 1964). Katayama and Trumbore (1964) attributed the relative reductions of G (hydrogen) by DPPH and iodine together with the insensitivity of G (hydrogen) toward temperature to one or more of the following mechanisms: (1) a hot (i.e. unscavengeable) hydrogen atom abstraction process, (2) a molecular elimination process, and/or (3) ion -

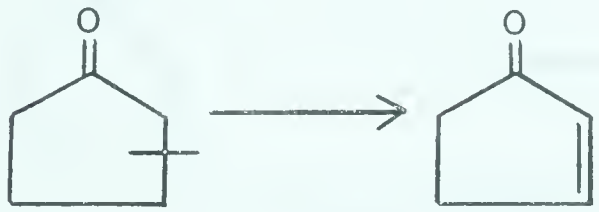
molecule reactions. Their mechanism for hydrogen formation is given in equations I-27 to I-30.



$$+ \quad H\cdot \qquad \text{(I-27)}$$



$$+ \quad H_2 \qquad \text{(I-28)}$$



$$+ \quad H\cdot \qquad \text{(I-29)}$$

$$H \quad + \quad$$



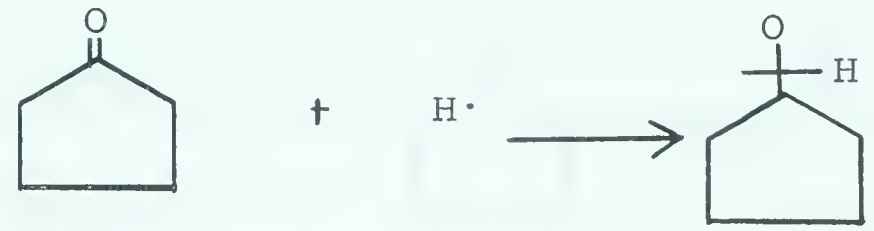
$$+ \quad H_2 \qquad \text{(I-30)}$$

The line drawn between carbons 2 and 3 in the above equations is used to show an unpaired electron which is associated with either one of the carbon atoms. Katayama and Trumbore also speculated that only 5% of the hydrogen resulted from thermal hydrogen atom abstraction reactions.

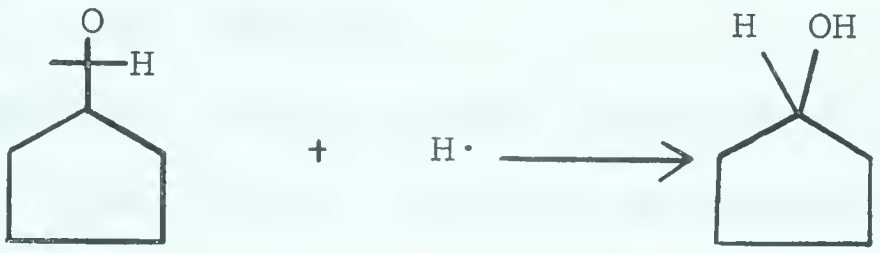
(2) Cyclopentanol

The radiolytic yield of cyclopentanol (0.81) was found to be constant up to a dose of 2×10^{20} eV/g at which point the yield began to decrease and a secondary product was observed (Bristowe, et al., 1964). These authors

also found that both DPPH and oxygen reduced the initial yield to zero. Cyclopentanol was postulated to arise from a stepwise addition of hydrogen atoms to a cyclopentanone molecule as shown in equations I-31 and I-32.



(I-31)



(I-32)

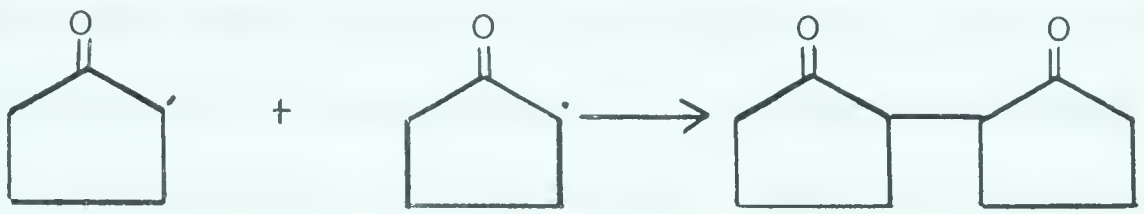
(3) Cyclopentenone

The radiolytic yield of cyclopentenone (0.21) was found to be constant up to a dose of about 1 x 10^{20} eV/g at which point the yield began to decrease due to secondary reactions (Bristowe, et al., 1964). The initial yield of this product was essentially unaffected by the addition of oxygen and DPPH. The effect of iodine on this product was not definite.

(4) Dimers

The yield of dimeric compounds (in arbitrary units) from the radiolysis of cyclopentanone was reported to increase rapidly at doses greater than 1.5 x 10^{20} eV/g (Bristowe, et al., 1964). This increase was partially offset by the decreasing yield of cyclopentenone at approximately the same dose. The dimer yield was quickly

reduced to zero by the addition of oxygen, DPPH, or iodine and the proposed mechanism of the formation of one of the three isomeric dimers is given in equation I-33.



(I-33)

(5) Polymer

Bristowe, et al. (1964) reported an initial 'polymer' yield of 4.4 (in units of monomer reacted to form polymer), which was independent of the absorbed dose. This value was calculated from the weight of the residue remaining in the radiolysis cell after evaporation of the volatile compounds in a vacuum system. Microanalyses from the polymer obtained at several doses showed no significant changes from the ketone composition. IR and NMR spectra indicated only that carbonyl groups and methylene groups were present and that some ring character had been retained.

b. Products Arising from C-C Bond Cleavage

(1) Carbon monoxide

The initial yield of carbon monoxide from the gamma radiolysis of cyclopentanone was reported to be 1.5 ± 0.3 (Katayama and Trumbore, 1964). They reported that the yield of this product decreased with increasing dose until reaching a constant value of 0.7 at a dose of

1×10^{20} eV/g and that the yield was essentially unaffected by slight changes in the surface area of the radiolysis cells. Increasing the temperature from 25° to 100°C caused a 33% increase in G (carbon monoxide) whereas decreasing the vapor space in the radiolysis cells caused a decreased yield. The effects on G (carbon monoxide) caused by changing the volume of the vapor or increasing the dose were suggested as evidence of the involvement of this product in the radical scavenging reaction shown in equation I-34.

$$R\cdot + CO \longrightarrow R\dot{C}O \qquad \text{(I-34)}$$

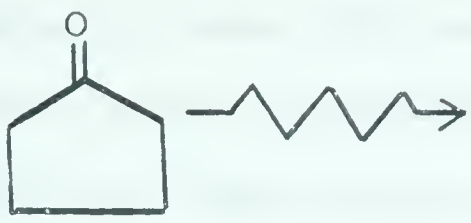
It has been previously postulated that carbon monoxide is capable of scavenging radicals (Ausloos and Trumbore, 1959).

The addition of DPPH or iodine caused essentially no change in G (carbon monoxide) whereas carbon dioxide or ethylene caused an increase of about 5%. As a result of these findings, Katayama and Trumbore (1964) concluded that the precursor of carbon monoxide is neither a readily scavengeable free radical nor a species which readily undergoes energy or charge transfer processes. They also suggested that the slight increase (which they reported) in G (carbon monoxide) from cyclopentanone solutions containing ethylene or carbon dioxide may be due to the scavenging action of these additives on a

radical which would otherwise be incorporated into polymer. The product of this radical-scavenger reaction might have a longer lifetime, thereby allowing a molecule of carbon monoxide to be lost before the residue was incorporated into polymer (Katayama and Trumbore, 1964).

(2) 4-Pentenal

Bristowe, et al. (1964) found a dose independent G value of 4-pentenal of 0.74. Their unirradiated cyclopentanone contained about 0.03% of 4-pentenal which represented about 30% of the concentration of this compound which they obtained at the highest dose used (2.5×10^{20} eV/g). A 20% reduction in the yield of the aldehyde from oxygen saturated cyclopentanone was also reported (Bristowe, et al., 1964). They stated that their results from solutions containing iodine or DPPH "were not consistent with the oxygen results", and that both DPPH and iodine might sensitize the formation of 4-pentenal. The effects of these additives were considered to be consistent with a mechanism whereby they prevented secondary reactions which might otherwise cause a destruction of the aldehyde (Bristowe, et al., 1964). As they pointed out, however, their linear dose-yield curve for 4-pentenal is difficult to understand in terms of such a mechanism. The mechanism which they proposed for the formation of 4-pentenal involves a concerted process as shown in equation I-35.



$$CH_2{=}CHCH_2CH_2CHO \qquad \text{(I-35)}$$

(3) Ethylene

Bristowe et al. (1964) have reported a dose-independent G value of ethylene of 0.85 which is unaffected by saturating the ketone with oxygen prior to radiolysis. They also found that 10^{-3}M concentrations of DPPH or iodine failed to affect the yield of this compound. These data coupled with the fact that the ethylene obtained from cyclopentanone-2,2,5,5-d_4 was about 90% CH_2CD_2 (Katayama and Trumbore, 1964) led Trumbore and coworkers to postulate that ethylene was formed by either a concerted decomposition of a cyclopentanone molecule or possibly by a biradical which decomposes too rapidly to be scavenged at these additive concentrations.

(4) Other minor products

Bristowe et al. (1964) reported the following initial yields for C_4 products from the radiolysis of cyclopentanone: cyclobutane (0.11), n-butane (0.050), and 1-butene (0.073). The yields of all three of the C_4 compounds were independent of dose. n-Butane was eliminated as a product by the addition of DPPH, oxygen and iodine. The yield of cyclobutane was found to be unaffected by added oxygen and was either unchanged or slightly increased by the other additives. The yield of 1-butene

was reduced by about 50% when the ketone was saturated with oxygen prior to radiolysis but DPPH and iodine did not affect it. From these results Bristowe *et al.* suggested that n-butane and 1-butene arise from the tetramethylene biradical and that cyclobutane is produced in a concerted process. These investigators also detected propylene as a product but no yield was given.

E. Radiolysis of Cyclohexanone

An extensive study on the radiolysis of pure cyclohexanone (Singh and Freeman, 1964a), and the effects of oxygen, 2,3-dimethyl-1,3-butadiene (DMB) and benzene on the yields of products arising from C-H bond breakage (Singh and Freeman, 1964b) have been reported. The effects of these three additives on the yields of products formed by cleavage of C-C bonds have been reported elsewhere (Singh, 1963).

1. Products Involving C-H Bond Cleavage

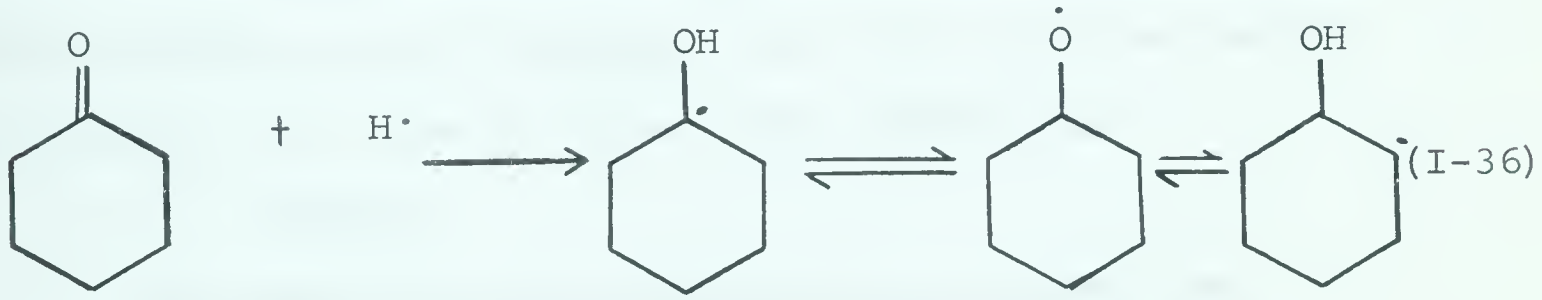
a. Hydrogen

Singh and Freeman (1964a) reported an initial hydrogen yield of 0.76. The yield decreased slightly with increasing dose. Both DMB and benzene inhibited the formation of hydrogen but the effect caused by DMB was more pronounced than that of benzene at concentrations less than 0.1 electron fraction (Singh and Freeman, 1964b). These authors postulated that benzene served to deactivate

an excited ketone molecule, thereby reducing the C-H bond scission, whereas the mechanism of hydrogen inhibition by DMB was more complex.

b. Cyclohexanol

Singh and Freeman (1964a) reported an initial yield of cyclohexanol of 0.5 and found that the yield increased with dose. Oxygen or DMB at concentrations of less than 1 mole per cent, reduced the yield of the alcohol to below the detection limit ($G < 0.2$), while benzene appeared to act only as a diluent (Singh and Freeman, 1964b). These results were considered to be consistent with a free radical mechanism for the formation of cyclohexanol involving H atom abstraction or disproportionation reactions of the species shown in equation I-36.



(I-36)

c. Cyclohexenone

The initial yield of cyclohexenone was reported to be 0.4, and the yield decreased with increasing dose (Singh and Freeman, 1964a). The effects of additives on the yield of this compound could not be determined because the yields were below the detection limit ($G < 0.2$) at the dose used for mixtures (Singh and Freeman, 1964b). Singh (1963) has postulated that cyclohexenone is formed

either by the molecular elimination of hydrogen from an excited ketone molecule or by the disproportionation of $C_6H_9O\cdot$ radicals.

d. Dimers

The initial yield of the total dimers formed from cyclohexanone has been reported to be 1.2 (Singh and Freeman, 1964a). The yield of these compounds was shown to decrease with increasing dose. The analogous radical to that shown in equation I-33 was suggested as the main source of the dimer (Singh and Freeman, 1964a). These authors also found that small quantities of oxygen or DMB reduced the total dimer yield to below the detection limit ($G < 0.2$) while the inhibition by benzene was much more gradual (Singh and Freeman, 1964b). These results are in agreement with the relative radical scavenging abilities of these three additives.

3. Polymer

The yield of chloroform soluble polymer from cyclohexanone has been found to increase with dose from an initial yield of 1.8 (in units of monomer reacted to form polymer) (Singh and Freeman, 1964a). Microanalysis of one polymer sample showed no compositional differences from cyclohexanone, but exhibited an average molecular weight between those of the "trimer" and "tetramer" (Singh and Freeman, 1964a).

Singh and Freeman (1964b) obtained microanalyses of the polymer from two samples that contained 0.3 electron fraction of DMB in cyclohexanone. These analyses showed that the polymer contained a 1:1 ratio of ketone:diene units and had an average molecular weight of 400 ± 30. They also found an iodine number of 138 ± 22. These data, together with the weight of polymer obtained and the rate of disappearance of DMBwere suggested as evidence for the reactions shown in equations I-37 and I-38.

$$R\cdot + CH_2{=}C(CH_3)-C(CH_3){=}CH_2 \longrightarrow \underset{I}{R-CH_2-C(CH_3)\dot{=}C(CH_3)\dot{=}CH_2} \qquad (I\text{-}37)$$

where R represents a C_6H_9O radical.

$$2\ I \longrightarrow \underset{II}{C_{24}H_{38}O_2} \qquad (I\text{-}38)$$

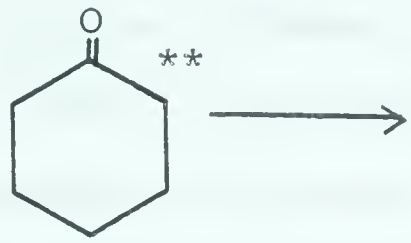
Compound II requires a molecular weight of 360 and an iodine number of 141 (Singh and Freeman, 1964b).

2. Products Involving C-C Bond Cleavage

a. Carbon Monoxide

The yield of carbon monoxide (G = 0.48) was found to be independent of dose (Singh and Freeman, 1964a). Singh (1963) found that the yields of this compound from solutions containing DMB or benzene showed only a diluent effect and the mechanism of formation proposed involved

either an excited cyclohexanone molecule or an excited biradical which liberates carbon monoxide too rapidly to be affected by the additives. These reactions are shown in equations I-39 and I-40.



$$\dot{C}H_2CH_2CH_2CH_2CH_2\dot{C}O^* \longrightarrow CO + \dot{C}H_2CH_2CH_2CH_2\dot{C}H_2 \quad (I\text{-}40)$$

b. Ethylene

The initial yield of this product was found to be 0.12 and the yield decreased with increasing dose (Singh, 1963). Addition of either DMB or benzene caused only a diluent effect on the G value of ethylene and this was attributed to the high excitation energy of the ketone molecule (or biradical) which was responsible for its formation.

c. 5-Hexenal

The radiolytic yield of 5-hexenal was found to decrease with increasing dose and the initial yield was reported to be 0.85 (Singh and Freeman, 1964a). Singh (1963) has reported that the addition of oxygen or DMB resulted in inhibition of the formation of this compound whereas benzene sensitized it. These results were suggested to be consistent with the formation of this product from a low-lying excited state which could readily

participate in energy transfer reactions with the additives. This mechanism will be considered more fully in the discussion of the present work.

d. C_5 Products

Singh and Freeman (1964a) reported the initial yields of four C_5 products from the radiolysis of cyclohexanone: 1-pentene (0.22), 2-pentene ($\sim$0.004), n-pentane (0.023), and cyclopentane (0.04). They found that the yields of all four compounds were independent of dose. Analytical difficulties prevented measuring yields of these compounds from DMB solutions. Benzene appeared to sensitize the formation of the straight chain compounds but to act only as a diluent on the yield of cyclopentanone. All four compounds were postulated to arise from the pentamethylene biradical (Singh, 1963).

A large number of other minor products were identified but their yields will not be considered here. (See Singh, 1963).

F. The Scope of the Present Work

The purpose of the present study was to determine whether the previously observed effects of Co^{60} γ-rays on cyclohexanone are characteristic of cyclic ketones, or whether they result from special properties associated with a C_6 ring compound.

The identities of the radiolysis products and the

yields of these products from pure cyclopentanone were determined as a function of dose. The effects of various additives on the yields of the products were also studied. In addition, several possible mechanisms which were suggested by the cyclohexanone results were tested.

II. EXPERIMENTAL

A. Apparatus

1. High Vacuum System

The high vacuum system used in this work (Figs. II 1, II 2, and II 3) was constructed of Pyrex glass mounted on a rigid frame of metal rods (sized 5' x 5' x 1') which was in turn bolted to a heavy wooden table.

All glassware incorporated into the high vacuum system was cleaned with a mixture of sulphuric and nitric acids (~1:1), thoroughly rinsed with water and finally rinsed with doubly distilled water.

Evacuation of the high vacuum system was accomplished by means of a Welch duo-seal, two stage, vacuum pump aided by a mercury diffusion pump. Approximate pressures in the system were monitored by a type GP-110 Pirani vacuum gauge from Consolidated Electrodynamics. Pressures less than 5 microns were determined by means of the combination Toepler pump-McLeod gauge shown in Fig. II 3.

a. Main Manifold

A diagram of this portion of the high vacuum system is shown in Fig. II 1. Apiezon grease was used in traps T1 and T2 and on stopcocks 2 and 3 which were the only stopcocks with 10 mm bores used. Silicone grease was used to lubricate all other stopcocks and the ground glass joints. Ether was used exclusively for cleaning the greased surfaces.

FIGURE II 1

Main Manifold

Figure not drawn to scale.

⊗ 1 - 19	:	Stopcock
	:	Ground glass joint
AM	:	Auxiliary manifold
M	:	Mercury manometer
MDP	:	Mercury diffusion pump
MP	:	Mechanical pump
RS	:	Reservoir system
T1 - T4	:	Traps
GAS	:	Gas analysis system
SC	:	Sample cells
GS1	:	Gas sampler
SB1 - SB3	:	Calibrated storage bulbs

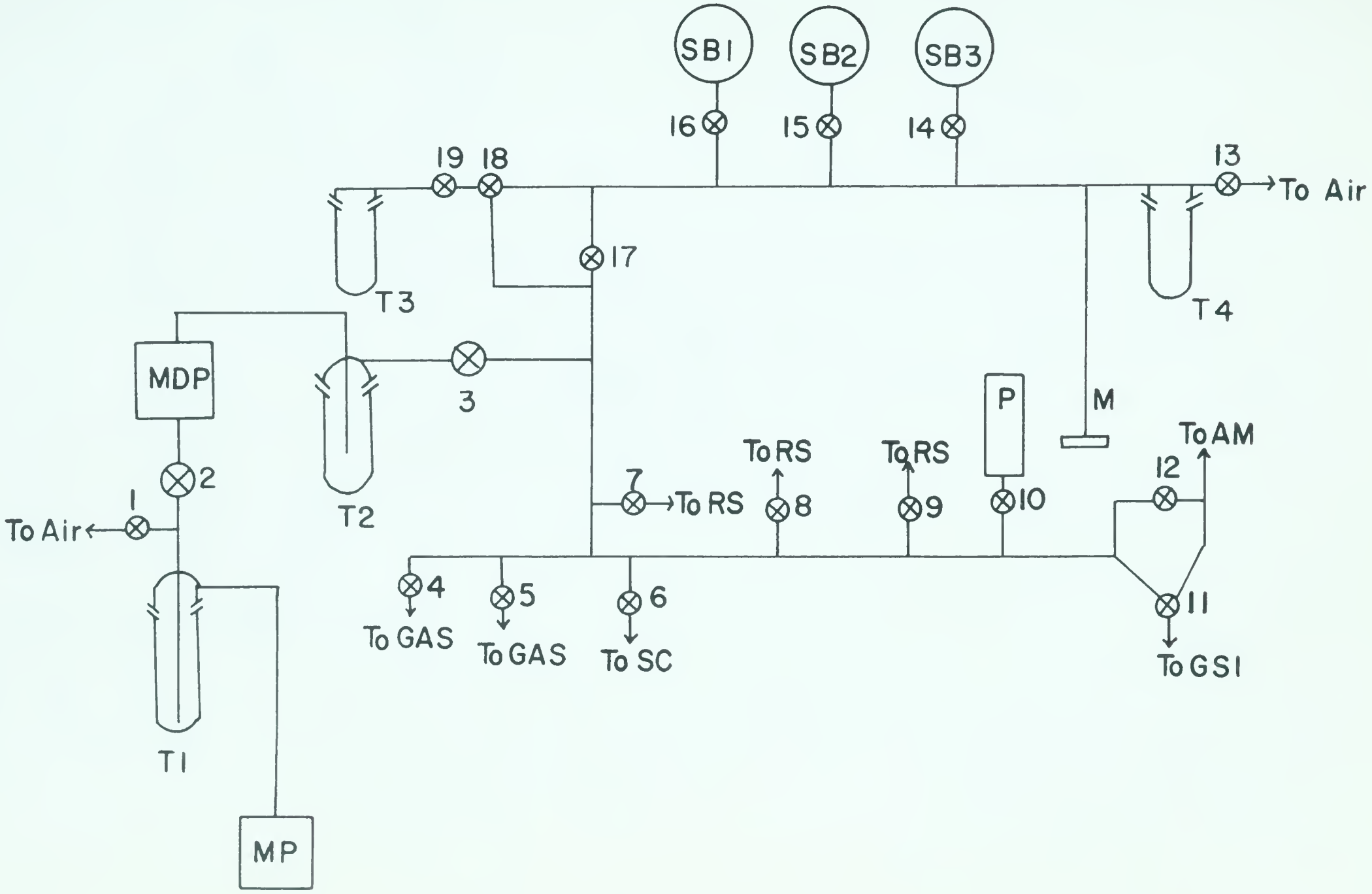

SB1
SB2
SB3
16
15
14
19
18
13
To Air
17
T3
T4
MDP
3
P
M
To AM
2
To RS
To RS
To RS
12
1
To Air
7
8
9
10
T2
4
5
6
11
To GAS
To GAS
To SC
To GSI
T1
MP

FIGURE II 2

Reservoir System.

Figure not drawn to scale.

⊗ 7 - 9,20 : Stopcock

B1 and B2 : Calibrated bulbs

FV1 - FV7 : Mercury float valves

R1 - R3 : Reservoirs

MM : Main manifold

M : Mercury manometer

MT1 - MT3 : Measuring tubes

SC : Sample cells

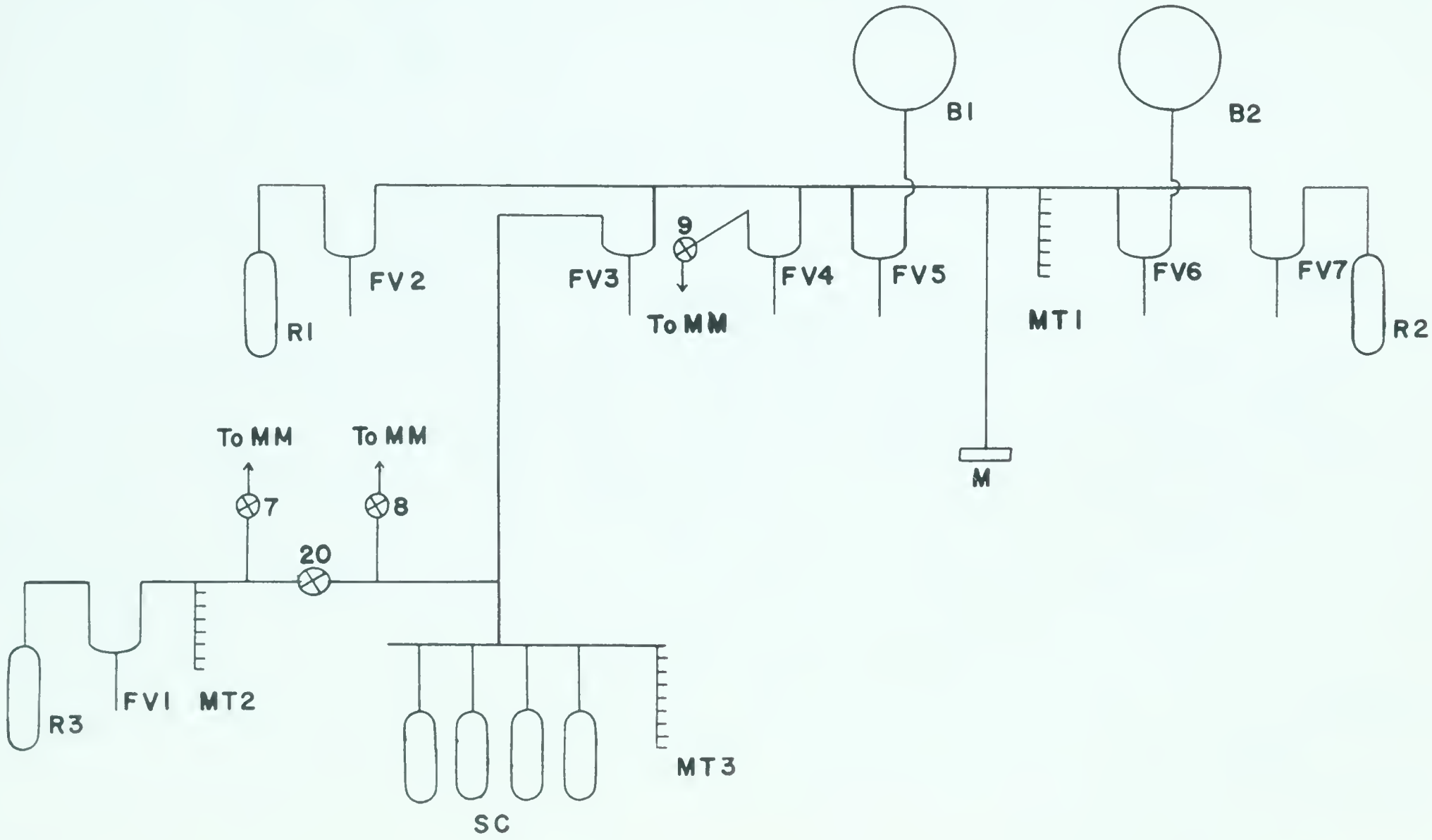
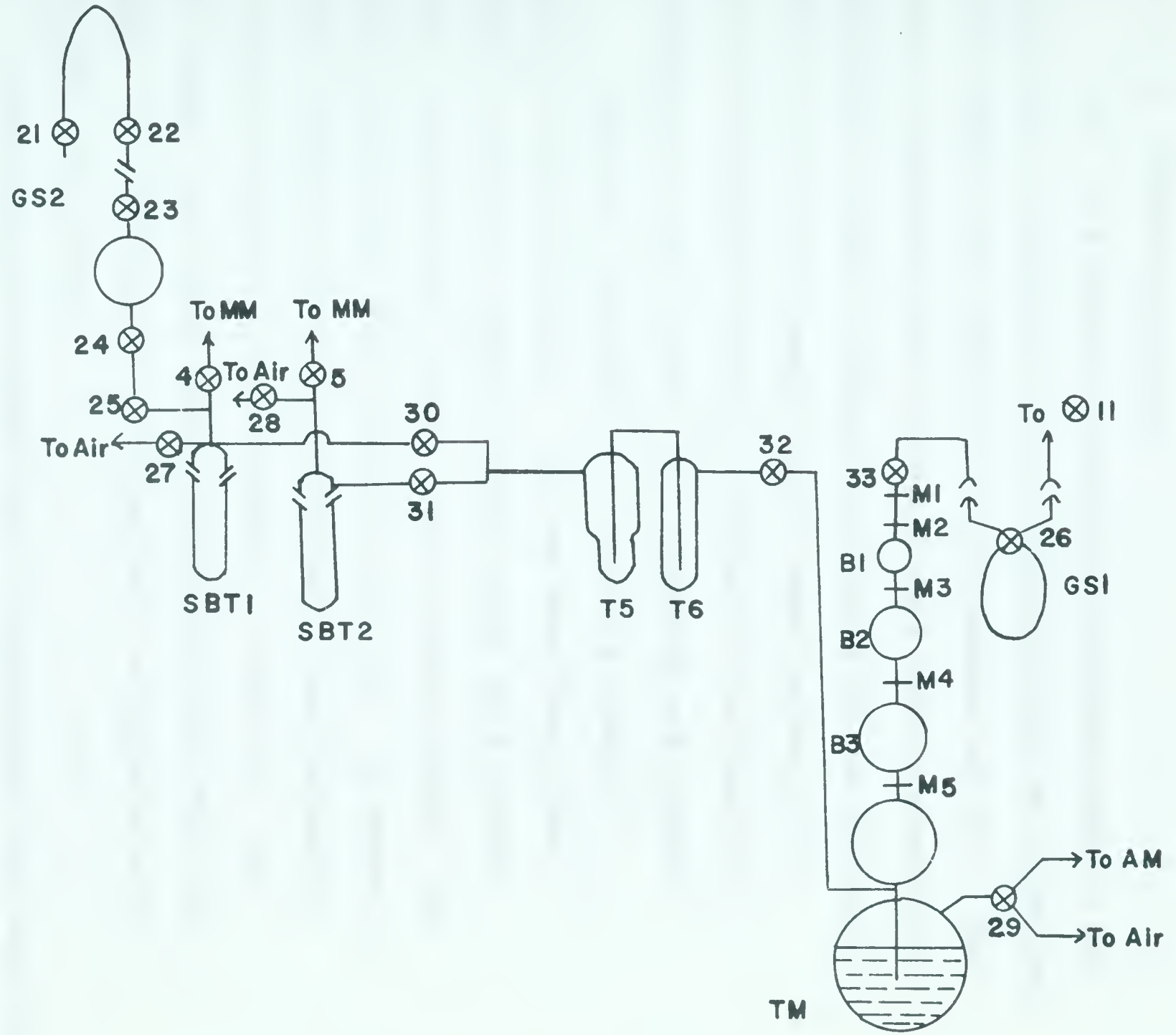

B1
B2
9
FV2
FV3
FV4
FV5
FV6
FV7
R1
To MM
MT1
R2
M
To MM
To MM
7
8
20
R3
FV1
MT2
MT3
SC

FIGURE II 3

Gas Measurement System

Figure not drawn to scale.

⊗ 21 - 35	:	Stopcock
	:	Ground glass joint
SBT1 - SBT2	:	Sample breaking trap
TM	:	Toepler - McLeod gauge
AM	:	Auxiliary manifold
GS1 - GS2	:	Gas sampler
RS	:	Reservoir system
T5 - T6	:	Traps
MM	:	Main manifold


21
22
GS2
23
24
25
To Air
27
To MM
To MM
4
To Air
5
28
30
31
32
SBT1
SBT2
T5
T6
To
11
33
M1
M2
B1
M3
B2
M4
B3
M5
26
GS1
To AM
29
To Air
TM

b. Reservoir System

Fig. II 2 shows the calibrated system used for the preparation of samples of pure cyclopentanone or solutions of the ketone with additives in the absence of air. The various compounds were introduced into their respective reservoirs through a stopcock connected to the system in place of one of the sample cells shown in Fig. II 2. After the compound had been isolated in its reservoir by means of a float valve, this stopcock was removed.

Measuring tubes MT2 and MT3 were used for measuring cyclopentanone. MT2 was made from glass tubing on which 45 equally spaced marks were etched using a diamond pencil and a metal cutting lathe. The volumes obtainable were 0.849 to 2.478 ml. In order to prepare samples containing additives it was necessary to measure ketone volumes as small as 0.040 ml. For this reason the second ketone measuring tube, MT3, was added. It consisted of a calibrated 1 ml pipette with divisions of 0.01 ml.

Quantities of benzene and 1,3-pentadiene were measured in the upper reservoir system shown in Fig. II 2, which consists of a manometer, six mercury float valves, measuring tube MT1 and calibrated bulbs B1 and B2. These bulbs had volumes of approximately 2 liters and 1 liter respectively. Measuring tube MT1 was prepared in the same way as MT2 and

had 27 equally spaced marks designating volumes of 1.143 to 2.114 ml. The six float valves and the manifold connecting them were calibrated prior to assembly. The volumes obtainable in this system are given in Table II 1.

Benzene was stored in reservoir R1 and pentadiene in reservoir R2 (Fig. II 2). Neither compound was allowed to come into contact with grease during measurement.

TABLE II 1

Calibrated Volumes of the Reservoir System.

Portion of system	Volume in liters
Manifold	0.171
Manifold + 1 liter bulb	1.31
Manifold + 2 liter bulb	2.33
Manifold + both bulbs	3.47

c. Gas Measurement System

Fig. II 3 shows the sample breaking traps (SBT1 and SBT2), distillation traps (T5 and T6), and the combined Toepler - McLeod gauge with attached gas sampler (GS1) which comprise this portion of the high vacuum system. Introduction of a float valve between bulbs 3 and 4 converted the gauge to a combination Toepler pump - McLeod gauge. The volumes of the Toepler - McLeod gauge corresponding to the marks shown in Fig. II 3 are given in Table II 2.

TABLE II 2

Calibrated Volumes of the Toepler - McLeod Gauge.

Mark	Volume in liters
M-1	0.344
M-2	0.674
M-3	2.51
M-4	5.95
M-5	9.02

The gas sampler (GS1) shown in Fig. II 3 was attached to the Toepler - McLeod gauge by means of 12/2 ball joints. The volume of gases isolated in the sampler was 12.88 ml and the geometry of the system was such that $\sim$ 70% of the gases collected in the gauge was available for analysis. The same gas sampler was used to collect both liquid nitrogen non-condensable and Dry Ice non-condensable gases. Between fractions, the sampler was thoroughly flushedwith air and evacuated by the high vacuum system.

Also shown in Fig. II 3 is a second gas sampler, GS2, which was used to introduce known gases into the gas analysis system. These gases were then transferred to gas sampler GS1 by means of the Toepler pump. Injection of these compounds on the gas chromatographic unit (GC) was accomplished by connecting the gas sampler (GS1) to the GC by means of the attached 12/2 ball joints

and rotating two four-way stopcocks. Since the gaseous products and the known compounds were injected on the GC columns by the same technique, identifications based on retention times were simplified.

d. Auxiliary Manifold

The auxiliary manifold was evacuated by a Welch duo seal two stage vacuum pump. The purpose of the auxiliary manifold was to operate the mercury cut offs and the Toepler - McLeod gauge. The mechanical pump was protected by a single uncooled trap which prevented mercury from polluting the pump oil.

2. Cobalt^{60} Sources

a. Source 1

Early irradiations were carried out in a heavy walled room in which a 300 curie Co^{60} source could be exposed. The source was confined to a lead and steel shield when not exposed. A steel track extending from the face of the shield together with a rigidly fixed pin at the end of the track, insured reproducible positioning of the source with respect to the samples. The source was attached to the end of a steel rod which extended from the back of the shield through one wall of the room. Placement of the source at a predetermined position along the track, and its subsequent withdrawal into the shield, was accomplished from outside the room. The sample containers (hereafter called blocks) were

located at rigid positions along the track. Blocks A and B were used for irradiations at room temperature and block C (Fig. II 4) was used for irradiations at approximately 120°C. In block C location of the samples was determined by holes drilled in the 2½ inch diameter solid aluminum cylinder. In blocks A and B, the samples were held in place by rigidly positioned glass tubes slightly larger in diameter than the sample cells. In block A, constructed by a colleague (Myron, 1960), the glass tubes were held in place by an aluminum frame. Block B (Wakeford, 1960) was a matrix of glass tubes held in a base of Wood's metal.

Source 1 was used for irradiating most of the pure cyclopentanone samples, all of the polymer cells, and all of the ketone samples irradiated at 120°C. It was also used to irradiate several cyclopentanone/benzene samples as part of a dose rate study, and a few liquid ketone samples containing oxygen.

b. Source 2

A Gammacell model 220 self shielding Co^{60} source with a strength of approximately 12,300 curies was obtained in 1963. Two blocks were used in this source. The first (block D) was an aluminum can ~2" in height and 6" in diameter to which a top and interior shelf had been welded (Fletcher, 1963). The top and shelf contained holes which were used to hold 2 ml liquid phase sample

FIGURE II 4

Heated Block for Liquid Samples.

AP : Aluminum plate

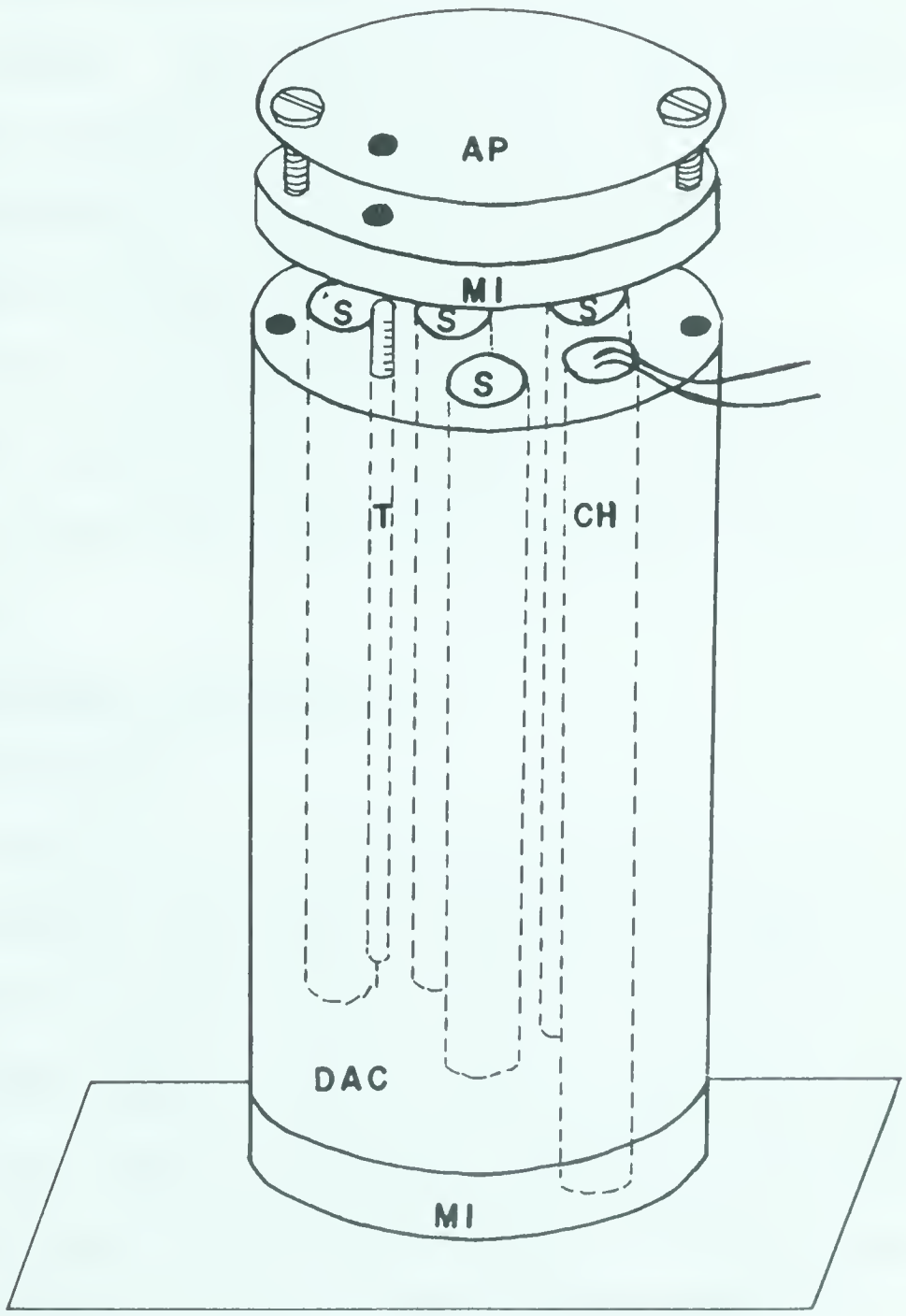
MI : Masonite insulator

S : Samples

CH : Chromolox heater

T : Thermometer

DAC : Drilled aluminum cylinder


AP
MI
S
S
S
S
T
CH
DAC
MI

cells. Only six of the fourteen positions located around the perimeter of the can were used for irradiations. The other block used in source 2, block E (Holtslander and Myron, 1963), was constructed of aluminum plates held together with bolts. Two heating tapes, sewn together in the shape of a sphere and fitted with an iron - constantan thermocouple, completed this block which was used for all 500 ml vapor phase samples.

Because of its higher dose rate and more homogeneous radiation field (as compared to source 1), source 2 was used for most of the cyclopentanone solutions containing liquid additives.

3. Analytical Instruments

a. Gas Analysis

A line diagram of the gas chromatographic unit (GC) used for analysis of gaseous products is shown in Fig. II 5. The hot wire detector (Model TR IIIB) and power supply (Model 9999 C) were obtained from the Gow Mac Instrument Co. and the recorder (cat. no. 347-01-25) was manufactured by E. H. Sargent and Co. Columns were constructed of either 1 meter or 2½ meter lengths of 3/8" heavy walled Pyrex tubing (C, Fig. II 5). The columns were heated by application of an A.C. potential to a nichrome wire wrapped around the column. The column was placed in a rectangular metal box packed with asbestos board and glass wool. Temperature measurement was

FIGURE II 5

Gas Chromatographic Unit Used for Analysis of Gases.

F : Flowmeter

D : Hot wire detector

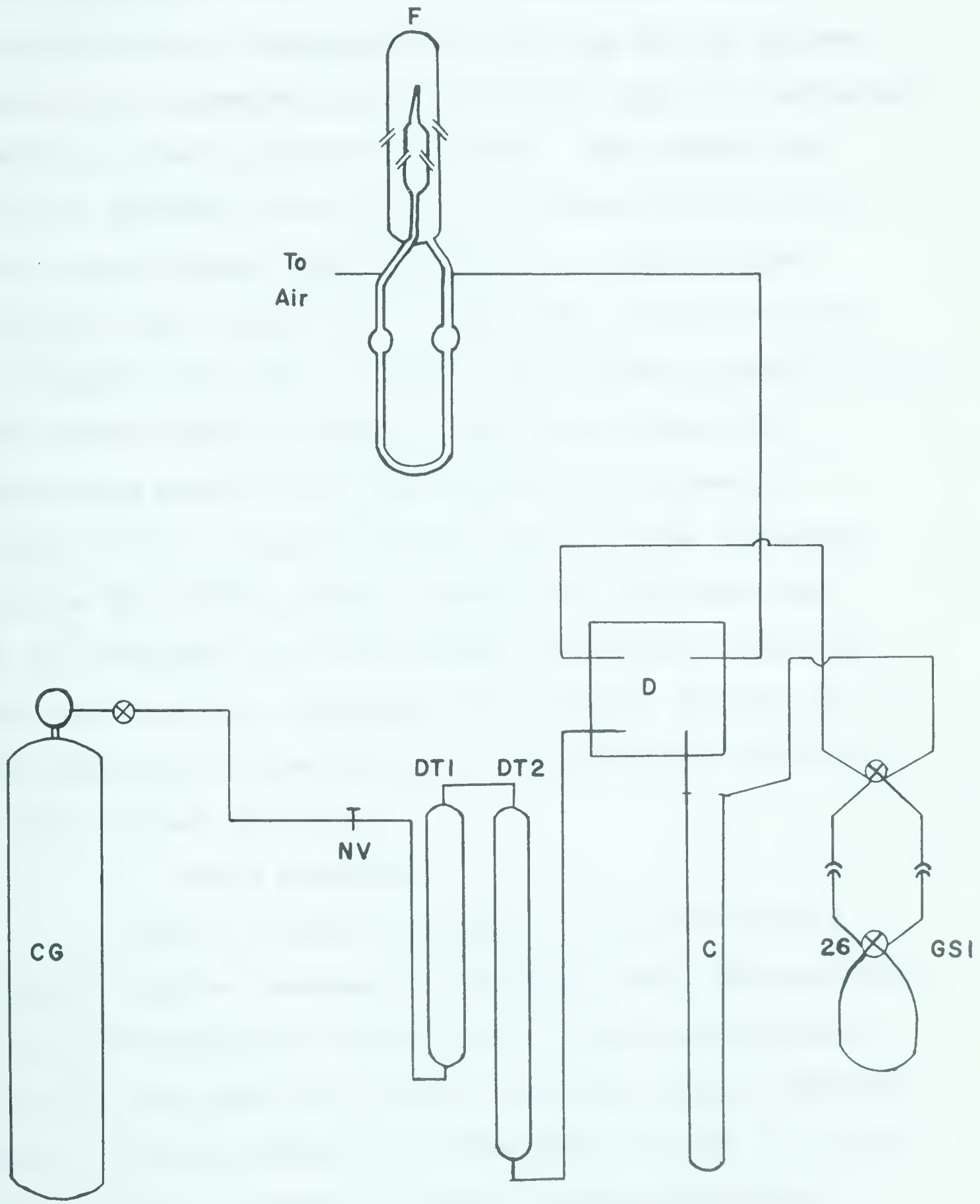
GS1 : Gas sampler

C : Column

DT1 and DT2 : Drying tubes

NV : Needle valve

CG : Carrier gas cylinder


F
To
Air
D
DT1
DT2
NV
CG
C
26
GS1

accomplished by means of a dial thermometer (Fisher Scientific Co.) introduced into the top of the columns so as to be immersed into the effluent gas at a sufficient depth to insure proper measurement. The carrier gas (either hydrogen or helium) at a pressure of 20 p.s.i. was passed through copper tubing to a needle valve (Edwards High Vacuum Ltd. - Type LB1A) which was used to regulate the flow. The gas then flowed through two drying tubes in series, the first filled with indicating Drierite and the second with Molecular sieves (13 X). Single stream flow was used, with the carrier gas first passing through the reference side of the detector and then through the column. Gas flow was monitored by a flowmeter (F) as shown in Fig. II 5. The detector was operated at a temperature of 210^{o}C and a cell current of 250 ma.

b. Liquid Analyses

A Burrell Kromo-Tog Model K2 was used for all liquid analyses, because it afforded a much more satisfactory chromatographic separation of the liquid products than was obtained with the gas analysis system described above. Columns similar to those shown in Fig. II 5 were used. A cell current of 235 ma was used throughout.

c. Ultraviolet Spectrophotometry

A Cary Recording Spectrophotometer (Model 14 M) was used for analyses in the visible and ultraviolet regions.

B. Materials

A list of most of the materials used is given in Table II 3. Unless otherwise stated, they were used as supplied.

TABLE II 3

Materials Used.

	Name	Source	Remarks (See after table)
1.	Acetylacetone	British Drug Houses (Canada) Ltd.	-
2.	Acetylene	Matheson of Canada Ltd.	-
3.	Allyl bromide	Fisher Scientific Co.	-
4.	Apiezon greases (L and N)	Metropolitan-Vickers Electrical Co., Ltd.	-
5.	Benzene	Phillips (Research grade)	i
6.	Bicyclopentyl-2,2'-dione	Prepared as described	ii
7.	n-Butane	Phillips (Research grade)	-
8.	1-Butene	Phillips (Research grade)	-
9.	cis-2-Butene	Phillips (Research grade)	-
10.	trans-2-Butene	Phillips (Research grade)	-
11.	Carbon dioxide	Matheson of Canada, Ltd.	-
12.	Carbon monoxide	Matheson of Canada Ltd.	-
13.	Carbowax 20M	F and M Scientific Corp.	-
14.	Celite (Kromat CE)	Burrell Corporation	-
15.	Charcoal	Burrell Corporation (high activity)	-

Table II 3, continued

	Name	Source	Remarks
16.	Chloroform	McArthur Chemical Co., Ltd.	-
17.	Cyclobutane	Research Council of Alberta	-
18.	Cyclobutanecarboxylic acid	Aldrich Chemical Co., Inc.	-
19.	Cyclopentane-1, 2-dione	Prepared as described	iii
20.	Cyclopentanol	Eastman Kodak (practical)	i
21.	Cyclopentanone	Eastman Kodak (White label)	iv
22.	2-Cyclopentenone	Sapon Laboratories	v
23.	Cyclopropane	Matheson, Coleman and Bell	-
24.	Di-iso-decyl phthalate	F and M Scientific Corp.	-
25.	Dimethyl sulpholane	F and M Scientific Corp.	-
26.	Di-n-decyl phthalate	Eastman Kodak (Practical)	-
27.	Dioxane	Fisher Scientific Co.	-
28.	Di-tert-butyl peroxide	Matheson, Coleman and Bell	-
29.	Drierite (8 mesh)	W. A. Hammond Drierite Co.	-
30.	Ethane	Phillips (Research grade)	-
31.	Ethylene	Phillips (Research grade)	-
32.	Ethylene glycol	Fisher Scientific Co.	-
33.	Ethyl vinyl ketone	K and K Laboratories, Inc.	-

Table II 3, continued

	Name	Source	Remarks
34.	Ferrous ammonium sulphate	Nichols Chemical Co., Ltd.	-
35.	Firebrick (Kromat FB)	Burrell Corporation	-
36.	Helium	Air Reduction Canada, Ltd. Matheson of Canada, Ltd.	- -
37.	Hydrogen	Canada Liquid Air	-
38.	Magnesium sulphate	Mallinckrodt	-
39.	Mercury	Mallinckrodt (Triple distilled)	-
40.	Methane	Phillips (Research grade)	-
41.	Methyl cyclopropane	Prepared as described	vi
42.	Molecular sieves (No. 13 X)	Burrell Corporation	-
43.	Nitric acid	Nichols Chemical Co., Ltd.	-
44.	Nitrogen	Air Reduction Canada, Ltd.	-
45.	Nonylphenoxy (polyethyleneoxy) ethanol	F and M Scientific Corp.	-
46.	Oxygen	Canadian Liquid Air	vii
47.	1,3-Pentadiene	Columbia Organic Chemicals Co., Inc.	viii
48.	1,5-Pentanediol	Eastman Kodak (Practical)	-
49.	3-Pentanone	Eastman Kodak (White label)	-
50.	4-Pentenal	Prepared as described	ix
51.	Phosphorus tribromide	Matheson, Coleman and Bell	-

Table II 3, continued

	Name	Source	Remarks
52.	Picien wax	Edwards High Vacuum, Ltd.	-
53.	Poly-m-phenyl ether	Wilkens Instrument and Research, Inc.	-
54.	Potassium dichromate	British Drug Houses (Canada) Ltd.	-
55.	Potassium hydroxide	Fisher Scientific Co.	-
56.	Potassium permanganate	Mallinckrodt	-
57.	Propane	Phillips (Research grade)	-
58.	Propylene	Phillips (Research grade)	-
59.	Selenious acid	Fisher Scientific Co.	-
60.	Silica gel	Burrell Corporation (medium activity)	-
61.	Silicone grease	Dow Corning	-
62.	Silicone rubber	Wilkens Instrument and Research, Inc.	-
63.	Sodium	British Drug Houses (Canada) Ltd.	-
64.	Sodium carbonate	Mallinckrodt	-
65.	Sodium chloride	Mallinckrodt	-
66.	Sodium sulphate	Mallinckrodt	-
67.	Sulphuric acid	Nichols Chemicals Co., Ltd.	-
68.	Ucon LB-1800-X	Carbide and Carbon Chemicals Co., Ltd.	-
69.	n-Valeraldehyde	Eastman Kodak (Practical)	-
70.	n-Valeric acid	Eastman Kodak (White label)	-
71.	Water	Doubly distilled	x

Remarks from Table II 3:

i. Distilled before use.

ii. Bicyclopentyl-2,2'-dione

This compound was prepared by the reaction of di-tertiary-butyl peroxide with cyclopentanone according to the directions given for cyclohexanone (Moore, 1951). This procedure was modified because the rate of decomposition of the peroxide at the boiling point of cyclopentanone would have been much slower than at the higher temperature obtainable in the case of cyclohexanone. Therefore, the reflux time was increased from two days to one week and the refluxing was carried out under an atmosphere of nitrogen. The straw yellow liquid collected (b.p. 134-138°/18-20 mm; lit. b.p. 124-128°/15 mm [Robinson and Hudson, 1951]) was shown by gas chromatography to contain approximately 85% bicyclopentyl-2,-2'-dione. The remaining 15% of the product consisted of two other "dimers" of cyclopentanone.

iii. Cyclopentane-1,2-dione

This compound was prepared by the method given for cyclohexane-1,2-dione (O.S. 32:35). The reaction is as follows:

$$C_5H_8O + H_2SeO_3 \longrightarrow C_5H_6O_2 + Se + 2H_2O$$

The material collected (b.p. 84-88°/15-18 mm; lit. 105°/20 mm; m.p. 55-56° [Hesse and Bücking, 1949]) resulted in white crystals upon recrystallization from cyclohexane.

The identity of this material was further substantiated by N.M.R. analysis (Bigam, 1964).

iv. Cyclopentanone

The material supplied contained water and cyclopentanol as its largest impurities. This mixture was distilled through a 45 cm column packed with glass helices. Anhydrous magnesium sulphate or sodium sulphate was added to the middle 50% of the distillate, and this material was stored in a stoppered flask in a desiccator for 48 hours prior to redistillation. The purified ketone used in most of the samples contained 0.007% 4-pentenal, 0.02% water, $<$0.001% cyclopentenone, and $<$0.004% cyclopentanol.

v. 2-Cyclopentenone was purified by bulb to bulb distillation in vacuo.

vi. Methylcyclopropane was prepared by the reaction of a zinc-copper amalgam with 1,3-dibromobutane.

vii. Oxygen was passed through a Dry Ice cooled trap prior to use to remove water vapor.

viii. 1,3-Pentadiene

The diene was first distilled under atmospheric pressure. It was then distilled under vacuum from a flask cooled in Dry Ice/carbon tetrachloride into reservoir R2 (Fig. II 2) cooled in liquid nitrogen. This procedure reduced the detectable impurities to less than 0.2% as shown by gas chromatographic analysis, and none of the

impurities interferred with product analyses.

ix. 4-Pentenal

This compound was prepared from ethylene glycol by the method described by Hurd and Pollack (1938). The reactions were as follows:

$$HOCH_2CH_2OH + Na \longrightarrow NaOCH_2CH_2OH + \tfrac{1}{2} H_2$$

$$CH_2{=}CHCH_2Br + NaOCH_2CH_2OH \longrightarrow NaBr + CH_2{=}CHCH_2OCH_2CH_2OH$$

$$3\ CH_2{=}CHCH_2OCH_2CH_2OH + PBr_3 \xrightarrow{C_5H_5N} 3CH_2{=}CHCH_2OCH_2CH_2Br + H_3PO_3$$

$$CH_2{=}CHCH_2OCH_2CH_2Br + KOH \longrightarrow CH_2{=}CHCH_2OCH{=}CH_2 + H_2O + KBr$$

$$CH_2{=}CHCH_2OCH\text{-}CH_2 \xrightarrow[\text{(hot tube)}]{250^{\circ}} CH_2{=}CHCH_2CH_2CHO$$

Approximately 5 ml of vile smelling colorless liquid was collected (b.p. 101-102°/690mm; lit 103-104°/749 mm [Hurd and Pollack, 1938]). The purity of this compound was found by GC to be >99%.

x. The water used for the preparation of the Fricke dosimeter and for rinsing all glassware was doubly distilled. The distillate from an alkaline permanganate solution was redistilled.

C. Procedure

1. Dosimetry

The Co^{60} gamma-ray beam was calibrated using the Fricke dosimeter, which consists of a dilute aqueous solution of sulphuric acid, ferrous ammonium sulphate,

and sodium chloride (Allen, 1961). The dosimetry cells were 15.0 ± 0.1 mm (outside diameter) Pyrex tubes with rounded bottoms. These cells were cleaned with a hot mixture of sulphuric and nitric acids, rinsed with doubly distilled water and dried before use. Each cell was covered with a glass cap after filling, to avoid atmospheric contamination. One blank (unirradiated cell) was run with each set of dosimetry samples. The concentration of ferric ions produced was determined by means of a Cary Recording Spectrophotometer using a 0.5 cm quartz cell.

The constants used in calculating the energy absorbed were:

$G_{Fe^{+++}} = 15.5$ and $\epsilon_{Fe^{+++}}$ (at 304 mμ and 25°C) = 2225.

Energy absorbed in eV/ml hour =

$$\frac{\text{Net O.D.} \times 6.023 \times 10^{25}}{T \times 2225 \left[1 + 0.007 \, (t^{o} - 25)\right] \times 15.5 \times 10^{3} \times D} \qquad \text{(II-1)}$$

where net O.D. is the optical density of the solution less the O.D. of the blank, T is the time of irradiation in hours and D is the cell thickness in cm.

Periodic adjustments of the dosimetry values for radioactive decay were calculated from the equation:

$$N/N_o = e^{-\lambda t} \qquad \text{(II-2)}$$

with $\lambda = 3.60 \times 10^{-4} \text{day}^{-1}$.

Calculation of the dose received by a sample was based on the ratio of the electron density of the ketone

to that of the Fricke dosimeter. To facilitate calculations of the doses received by mixtures of cyclopentanone with additives, the dose rates were calculated in eV/e^- hour using the electron density of the Fricke dosimeter (0.566 mole e^-/ml). Equal irradiation times in a given position insured that the energy absorbed by the ketone in each sample was the same.

Dose rates given in the following table (Table II 4) were standardized to May 1, 1964 to facilitate comparison.

TABLE II 4

Dosimetry Values.[a]

Source	Block	Position in block	Volume of solution in ml	Energy absorbed (10^{-5} eV/e^- hr)
1	A	12	2	0.74*
1	A	13	2	1.12
1	A	14	2	1.55
1	A	15	2	1.51
1	A	16	2	1.09
1	A	17	2	0.66*
1	A	20	2	0.63*
1	A	24	2	0.58*
1	A	13	10	0.82*
1	A	14	10	1.05*
1	A	15	10	0.96*
1	A	16	10	0.74*

Table II 4, continued

Source	Block	Position in block	Volume of solution in ml	Energy absorbed (10^{-5} eV/e^- hr)
1	B	1	2	1.88
1	B	2	2	1.56
1	B	3	2	1.37
1	B	4	2	1.42
1	B	5	2	1.82
1	B	7	2	0.70
1	B	8	2	0.66
1	B	9	2	0.63
1	B	10	2	0.64
1	B	1	10	1.23
1	B	2	10	1.04
1	B	3	10	0.92
1	B	4	10	0.95
1	B	5	10	1.13
1	C	1	2	2.88
1	C	2	2	1.42
1	C	3	2	1.47
1	C	4	2	1.50
2	D	1	2	15.9
2	D	3	2	15.7
2	D	5	2	15.8
2	D	8	2	15.7

Table II 4, continued

Source	Block	Position in block	Volume of solution in ml	Energy absorbed (10^{-5} eV/e^- hr)
2	D	11	2	15.9
2	D	13	2	16.1

* Values obtained from a coworker (Myron, 1960).

a: For purposes of comparison, a dose rate of 1.00×10^{-5} eV/e^- hr is equal to 3.11×10^{18} eV/ml hr for cyclopentanone.

The energy absorbed by the 500 ml vapor samples irradiated in source 2 was calculated using the average dose rate received by the 2 ml liquid samples. This value is about 5% lower than the average dose rate obtained by coworkers using ethylene dosimetry.

2. Preparation of Samples for Irradiation

Traps T1 and T2 (Fig. II 1) were always cooled in liquid nitrogen before starting the mechanical and diffusion pumps.

a. Storage and Degassing of Liquids

(1) Cyclopentanone

About 100 ml of doubly distilled cyclopentanone in a 250 ml round bottom flask with a 14/20 joint was attached to a stopcock on the sample cell manifold immediately after distillation. After pumping on the liquid for a period of 10-15 seconds, during which time several milliliters of the

ketone were lost, liquid nitrogen was placed around the flask and evacuation continued until a pressure of ~15 microns was registered on the Pirani gauge. The stopcock was then closed and the ketone was allowed to thaw slowly because of the effervescence resulting from the trapped air. After all of the ketone had been liquified, liquid nitrogen was again placed around the flask and pumping resumed. Three such operations with liquid nitrogen preceded distillation of the ketone into a reservoir (R3) that was protected by a mercury float valve (FV1, Fig. II 2). Once in the reservoir, at least seven more degassing cycles were carried out using liquid nitrogen as the freezing agent and then about five cycles using a Dry Ice/ethanol bath (-80^{o}C). The 2 ml blanks (unirradiated samples) of cyclopentanone treated in this manner, gave Toepler - McLeod readings of less than 1.0 mm at Mark 1 (0.344 ml) for both gaseous fractions. This amount of gas was usually completely negligible by comparison with amounts generated during radiolysis (e.g. 180 mm at 0.344 ml at a dose of 2×10^{20} eV).

The only samples filled with cyclopentanone not treated in this manner were those used for polymer estimation. These samples (either pure ketone or ketone mixed with 1,3-pentadiene) were pipetted directly into the sample cells and degassed at liquid nitrogen temperature (-196^{o}C).

(2) Benzene

Freshly distilled benzene (50 ml) was handled in the same manner as the cyclopentanone in the preceding section and stored in reservoir R1 (Fig. II 2).

(3) 1,3-Pentadiene

Freshly distilled 1,3-pentadiene (75 ml) was collected in a 125 ml flask and connected to the sample cell manifold in the above manner. After preliminary degassing by means of the freezing, pumping, thawing cycles used for all liquids, the diene was distilled into reservoir R2 (Fig. II 2). The reservoir was cooled with liquid nitrogen but the flask from which the diene was distilled was cooled to -25°C and only 2/3 of the liquid was distilled before the float valve (FV7) was closed. This distillation procedure was designed to prevent the introduction of polymeric materials into the reservoir.

b. Construction and Filling of Sample Cells

(1) Construction of cells for liquid samples

Cells were prepared from Pyrex tubing, the outer diameter of which was $\sim$0.1 mm less than the diameter of the cavities in the blocks in which the irradiations were performed. These diameters were from 15.0 to 15.2 mm. Lengths of Pyrex tubing were cleaned by sealing off one end and filling them with a mixture of sulphuric and nitric acids ($\sim$1:1) which was heated to boiling three

times. After thoroughly rinsing the tube with doubly distilled water it was constricted into three inch lengths which were then sealed off in pairs and kept until needed. All glassblowing involving the sample cells was done with air filtered through silica gel and/or Drierite to prevent contamination. The sample cells were separated and attached to the ¼" medium wall tubing previously attached to the sample manifold and the cell bottoms were then rounded off. One of the 2 ml sample cells used for analyses is shown in the sample breaking trap (Fig. II 6A) and another diagram shows the sample cells in position on the sample filling manifold (Fig. II 2). The sample cells contained roughly equal volumes of liquid and vapor.

Cells used for polymer analyses were of two types. The first was a longer version of that shown in Fig. II 6A so that it could accomodate 10 ml of liquid. The total volumes were $\sim$20 ml, and these were used for most polymer work. Some of the samples used for microanalyses were of the design shown in Fig. II 6B. This design was previously used by a colleague (Singh, 1961). The loop of 3/8" heavy walled tubing was incorporated to prevent glass chips from the break-seal from contaminating samples sent for analyses.

(2) Construction of bulbs for vapor samples

The vapor samples were prepared from 500 ml bulbs

FIGURE II 6

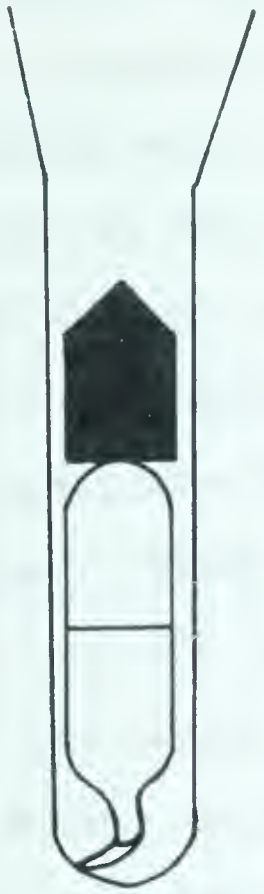
Liquid and Vapor Sample Cells.

A. Cell for 2 ml liquid samples (total volume about 4 ml) shown in breaking trap

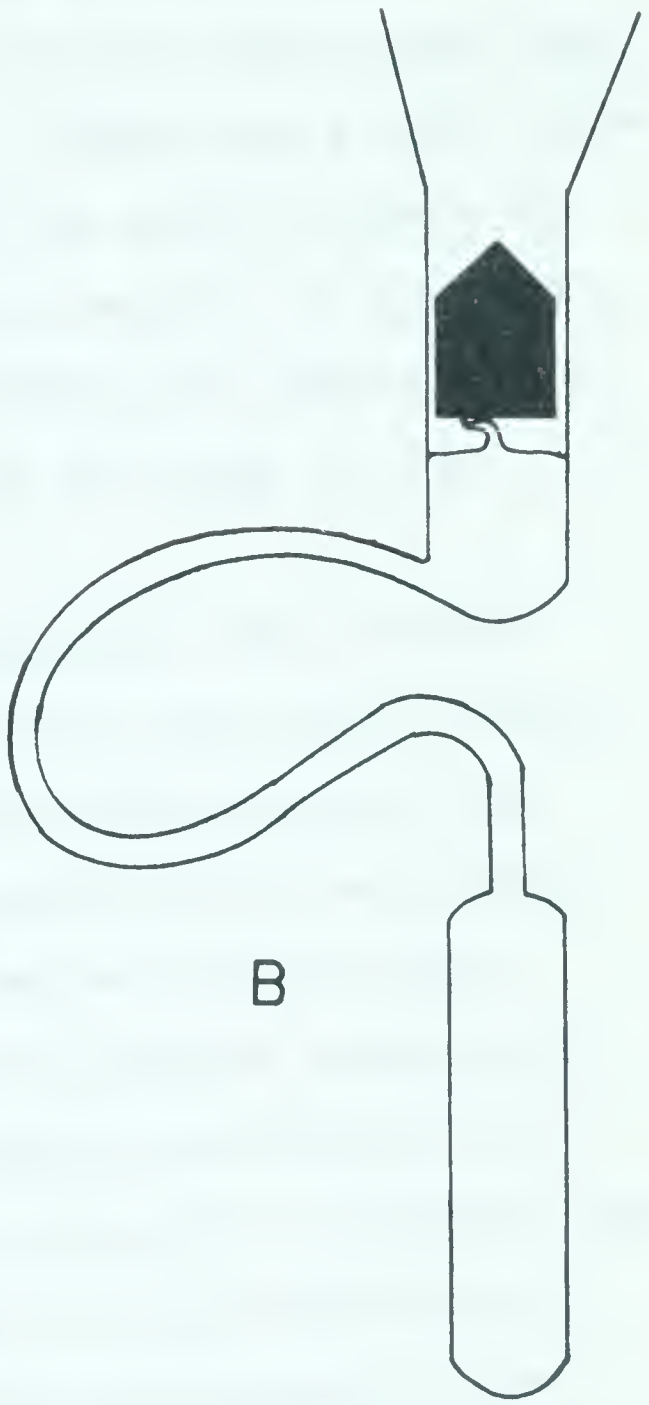
B. One type of cell used for the estimation of polymer yields from 10 ml samples (Total volume of cell is about 20 ml)

C. 500 ml bulb used for vapor phase samples

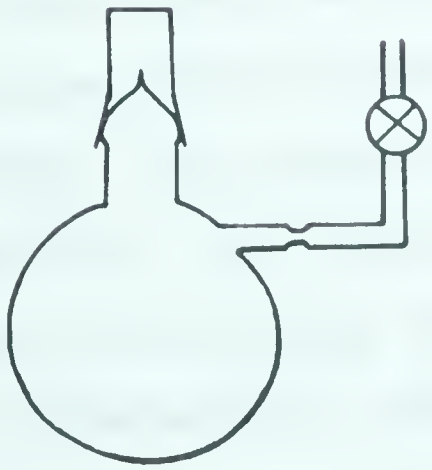
The metal breaking weight is shown in figures A and B.



A



B



C

with overall heights governed by the size of the sample chamber in source 2. The constricted side arm was used for sealing off the bulb after filling and a 14/20 inner joint fitted with a break-seal was used to attach the cell to the gas analysis system (see Fig. II 6C). The cleaning procedure was that afforded all quantitative glassware. The bulb design was developed in this laboratory (Myron, 1963).

(3) Filling of liquid or vapor samples

All cells were heated with a hand torch several times during evacuation until no deflection of the Pirani gauge was noted. Any cells not filled within 1½ days after mounting were removed and discarded.

Cyclopentanone was distilled from reservoir R3 into measuring tube MT2 for samples containing 1-2 ml of the ketone, or to measuring tube MT3 if volumes less than 1 ml were desired. About ¼ ml of the ketone in excess of the volume desired was distilled into the measuring tube and the volume sought was then obtained by evacuation. The volume of the ketone was usually measured at 0°C. The density of cyclopentanone at this temperature is 0.968 g/ml while at 30°C the density is 0.939 g/ml (Timmermans, 1950). Additional densities were obtained by a linear interpolation between these values. Corrections were applied for the cyclopentanone vapor assuming a vapor pressure of 5 mm at 0°C. (The

vapor pressure at 25°C is 11 mm).

Solutions of benzene and cyclopentanone were prepared by measuring the benzene as a gas for samples containing less than 40 per cent benzene and as a combination of liquid and vapor for the more concentrated samples. The limiting factor was the vapor pressure of the hydrocarbon which is 100 mm at 26.1°C. The density of liquid benzene at various temperatures was calculated from an empirical equation (Brunel and Van Bibber, 1928).

1,3-Pentadiene was measured as a vapor for all samples except those prepared for polymer determination, in which case the diene was measured with a calibrated syringe or pipette.

To prepare solutions of the diene in cyclopentanone in which the mole fraction of the di-olefin was very small (e.g. 3×10^{-4}), an expansion technique was used. The gas was originally confined to the reservoir system manifold (171 ml, Table II 1). Two float valves (FV5 and FV6, Fig. II 2) were then opened allowing the gas to expand into the calibrated bulbs B1 and B2. The float valves were then closed and the gas remaining in the manifold was distilled into the sample cell. A ten minute period was allowed for all expansions or distillations to establish equilibrium or to insure completion of distillation into the sample cells. After an additive had been measured in the calibrated portion

of the reservoir system, it was distilled into the sample cell which had been cooled with liquid nitrogen, by opening float valve FV3 (Fig. II 2).

Samples containing oxygen were prepared by freezing the cyclopentanone into a bulb or vial with a Dry Ice/ethanol mixture, closing the stopcock to the pump (⊠ 3, Fig. II 1), and reading the mercury manometer. Oxygen was then flushed through a Dry Ice cooled trap into the system, and excess oxygen was removed through the auxiliary manifold. After equilibrium was attained the final manometer reading was taken and the cell was flamed off.

3. Separation and Identification of Products

a. Gas Chromatography Columns

GC column packings were prepared by a gradual evaporation of the solvent from a stirred slurry containing the solid support and the partitioning agent in a suitable organic solvent. A list of the columns used in attempts to obtain optimum separations of the radiolytic products present is presented in Table II 5. Each column was used with a variety of flow rates and temperatures.

b. Gaseous Products

After the neck of a sample had been scratched to facilitate breaking, it was inverted and placed in a heavy walled Pyrex breaking trap fitted with a 24/40 outer joint. A mild steel weight was rested on the cell

TABLE II 5

GC Columns Used

Column[a]	Length in meters	Products for which separation was attempted
Charcoal (High Activity) *	1	H_2 and C_1
Silica gel (Medium Activity) *	2½	C_2 to C_4
Dimethyl sulpholane (40%) * on firebrick	2½	C_2 to C_4
Di-n-decyl phthalate (25%) on Celite	2½	C_5
Ucon LB-1800-X (25%) * on Celite	2½	C_5
Carbowax 20M (25%) * on Celite	2½	C_5
Nonylphenoxy-polyethylene-oxy-ethanol (25%) on Celite	2½	C_5
Tri-m-tolyl phosphate (25%) on Celite	2½	C_5
Di-iso-decyl phthalate (30%) on Celite	2½	C_5
Poly-m-phenyl ether (25%) on Celite	2½	C_5
Silicone grease (25%) * on Celite	2½	C_{10}
Silicone rubber (25%) * on Celite	2½	C_{10}
Apiezon L (25%) on Celite*	2½	C_{10}

a: All concentrations are given in the number of grams of partitioning agent per 100 grams of packing.

* Columns used for quantitative results which will be referred to hereafter only by the name of the partitioning agent.

bottom (see Fig. II 6A). The breaking trap (e.g. SBT1) was then attached to the gas analysis system (Fig. II 3) and the Toepler-McLeod and all traps were evacuated. After the pressure was reduced to about 1 μ, the stopcock to the main manifold (⊠4) was closed and further evacuation was carried out by means of the Toepler pump. The pressure was reduced to a point at which six consecutive pumping cycles failed to cause a non-zero reading on the smallest volume in the McLeod gauge. The stopcock separating the distillation traps from the sample breaking trap (⊠30) and that leading to the Toepler-McLeod (⊠32) were then closed and liquid nitrogen was placed around all three traps. After the sample had been cooled, the nitrogen around the breaking trap was removed. The sample was broken by dropping the steel weight on it by means of an external magnet. After a short pause, the stopcocks leading into the Toepler-McLeod (⊠30 and ⊠32) were opened and distillation of the sample began. Pumping was continued after all of the sample was distilled out of the breaking trap and until no more gases were collected. The stopcock to the Toepler-McLeod (⊠32) was then closed and the radiolyzed liquid was distilled back into the breaking trap. This procedure was repeated and the total quantity of gases collected while the distillation traps were cooled in liquid nitrogen will hereafter be referred to as the -196^{o} fraction. After recording the total quantity of gases collected in the Toepler-McLeod, the gases were transferred to the previously evacuated sampler (GS1, Fig. II 3) and were then injected on the GC. Hydrogen, carbon monoxide, and methane were found to be the only products

present in the -196° fraction by repeated injections of the radiolysis products on the charcoal column followed by injections of these three compounds on the G C under the same conditions.

A second gaseous fraction was collected in a similar manner using Dry Ice/ethanol (-80°C), ethanol slush (-112°C), or isopentane slush (-160°C) as the fractionating agent. For samples containing 1,3-pentadiene, the isopentane slush was always used. Ethanol or isopentane slush baths were used for samples containing benzene while samples of pure cyclopentanone were distilled through the Dry Ice/ethanol baths.

The compounds present in the -80° or -112° fractions were identified on the basis of retention times, on two columns of different separation characteristics. The first of these was the silica gel column which was temperature programmed and the second was a dimethyl sulpholane (DMS) column which was operated at room temperature. The main advantage of the silica gel column was that greater variation in retention times was possible by temperature programming, thus facilitating identifications. It did not separate n-butane from cyclobutane, however. A list of the retention times obtained for the products in the -80° and -112° fractions using the dimethyl sulpholane column at room temperature and with a flow rate of 43 ml of hydrogen/minute is given in Table II 6. The -160° fraction contained only ethane, ethylene, and traces of propylene.

TABLE II 6

Relative Retention Times of Products on DMS.*

Product Identified	Retention Time (min.)	Relative Retention Time	Relative Retention Time (Hively, 1960)
Ethane	0.96	0	0.004
Ethylene	1.1**	0.006	0.006
Propane	1.3	0.012	0.013
Carbon dioxide	1.3	0.012	-
Propylene	1.5	0.022	0.023
n-Butane	1.9	0.038	0.038
Acetylene	2.2	0.050	0.049
1-Butene	2.5	0.062	0.061
Methylcyclopropane	3.1	0.084	-
Cyclobutane	3.7**	0.111	-
1,3-Butadiene	4.4	0.138	0.136

* This column was used at 25°C with a flow rate of 43 ml (hydrogen)/min.

** These compounds were used as standards.

Compounds remaining in the system after removal of the gaseous products were usually discarded. Exceptions were the vapor samples and liquid phase cyclopentanone/oxygen samples on which liquid product analyses were also performed.

c. C_5 and C_{10} Products

For analysis of C_5 and C_{10} products, a separate set of samples was usually prepared and these samples were opened immediately before analysis. Samples of radiolyzed cyclopentanone were stored in polyethylene stoppered glass vials in a desiccator between injections. Samples which contained benzene or pentadiene were kept in glass vials fitted with corks wrapped in aluminum foil and were placed in separate desiccators.

Identifications of the liquid products from pure cyclopentanone were made by injecting 100 μl aliquots of an irradiated sample on at least two GC columns followed by injecting these same samples containing traces of the suspected products on the GC under the same conditions. If the product peak grew as a result of this treatment, analytical conditions were varied in an attempt to achieve a separation of the product and additive peaks. After all such attempts had failed, the identity of the compound was confirmed. Cyclopentanol, 4-pentenal, 2-cyclopentenone, and bicyclopentyl-2,2'-dione were found among the products by this method. The production of 3-cyclopentenone could

not be proved or disproved on the basis of this study.

Whenever other closely related compounds were obtained, a further check was made to prove whether they too could be products. A large number of analytical conditions were required to eliminate ethyl vinyl ketone, 3-pentanone, and n-valeraldehyde as additional products.

C_5 analyses were carried out on the Ucon LB-1800-X and Carbowax 20M columns listed in Table II 5. Analyses of the C_{10} products were performed on the Silicone grease and Apiezon L columns.

The addition of oxygen to liquid and vapor phase cyclopentanone samples led to the formation of several new compounds. Two of these were identified as cyclopentane-1,2-dione and n-valeric acid on the basis of their retention times on the Apiezon L and Silicone grease columns. The other products were produced in small yields and their retention times on the GC did not correspond to any of the compounds available. The radiolytic formation of a cyclohexanedione (and/or an hydroxycyclohexanone) has been reported from liquid phase cyclohexanone samples containing oxygen (Singh, 1963).

d. Polymer (excluding dimers)

Ten ml samples of pure cyclopentanone or cyclopentanone containing 1,3-pentadiene were irradiated in source 1, and care was taken to prevent inversion of

these samples after filling (until they were opened for analysis). After opening, the bulk of the C_5 compounds were removed by evaporation in the vacuum system. The cell was then removed from the system and thoroughly rinsed with three portions of low residue chloroform, dried by evacuation, and reweighed. The weight difference corresponded to the weight of C_5, C_{10}, and chloroform soluble polymeric compounds extracted from the cell. The chloroform rinses were combined in a tared 10 ml glass stoppered volumetric flask, and the weight of the chloroform solution was recorded. The C_5 and C_{10} content of the solution was determined by GC analysis and the weight of the polymer was determined by difference. Samples sent for microanalyses were handled in the same manner, and the chloroform solutions were then placed in cells fitted with ground glass joints. After the solvent had been largely removed by evacuation at room temperature, the cells were cooled in liquid nitrogen, and the tops flamed off. The residual chloroform content of each cell was determined by the analysis of the chlorine content of the material analyzed. The molecular weights of the mixtures analyzed were obtained by the m.p. depression of camphor (Rast method). The olefin content was measured by the reaction of the compounds with methyl magnesium iodide in a methanol solution. All microanalyses were

obtained from samples sent to West Germany (Pascher and Pascher, 1963, 1964).

4. Quantitative GC Analyses

a. Conditions of the GC Analyses

A list of the chromatographic columns used together with the analytical conditions employed is presented in Table II 7.

b. Calibrations of Gaseous Products

All gaseous products were calibrated separately. Gases were introduced into the gas measurement system (shown in Fig. II 3) by means of a gas sampler (GS2). It was possible, by an expansion technique, to introduce small quantities of a gas into the Toepler - McLeod gauge. After measuring the amount of the gas, it was transferred to an evacuated gas sampler (GS1) which was then attached to the GC apparatus (see Fig. II 5). Injection on the column was accomplished by opening two 4-way stopcocks. The calibration curves for the gases were constructed by plotting the peak height (for hydrogen) or the peak area (for all other gases) against the number of molecules injected on the GC apparatus. All of the calibration curves determined for gases were linear except that for hydrogen. Typical calibration curves for hydrogen and carbon monoxide are presented in Fig. II 7 and II 8 respectively. These data are also presented in Tables II 8 and II 9.

TABLE II 7

GC Columns Used for Quantitative Analyses and Conditions.

Column[a]	Products Analyzed	Temperature Range (°C)	Carrier Gas and Flow rate (in ml per minute)
Charcoal	H_2, CO, CH_4	50	Helium (48)
Silica gel	C_2 to C_4	25 - 160	Hydrogen (80)
DMS	C_2 to C_4	25	Hydrogen (43)
Carbowax[b]	C_5	90 - 130	Hydrogen (150)
Ucon[b,c]	C_5	130	Hydrogen (150)
Silicone grease	C_{10}	25 - 240	Hydrogen (100)
Apiezon L	C_{10}	25 - 220	Hydrogen (100)

a: Concentrations of the partitioning agents are given in Table II 5.

b: These columns were also used to determine the disappearance of 1,3-pentadiene.

c: Separation of cyclopentanol and 2-cyclopentenone was obtained only on the Carbowax column.

FIGURE II 7

Hydrogen Calibration

Peak Height (unit, 1/50")

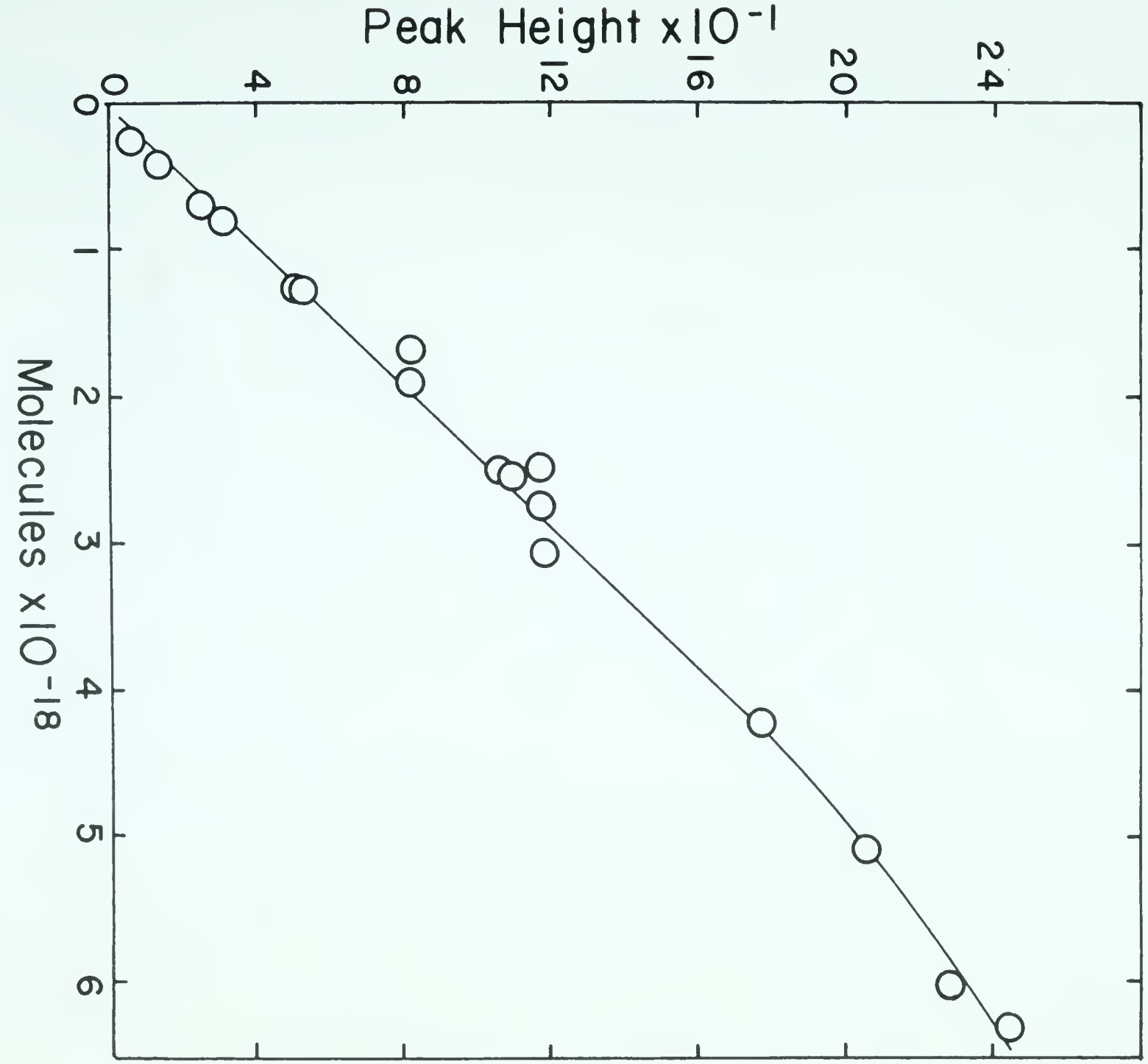

Peak Height x10⁻¹
0
4
8
12
16
20
24
Molecules x10-18
0
1
2
3
4
5
6

FIGURE II 8

Carbon Monoxide Calibration.

P.A. = Peak Area [unit, $(1/50")^2$]

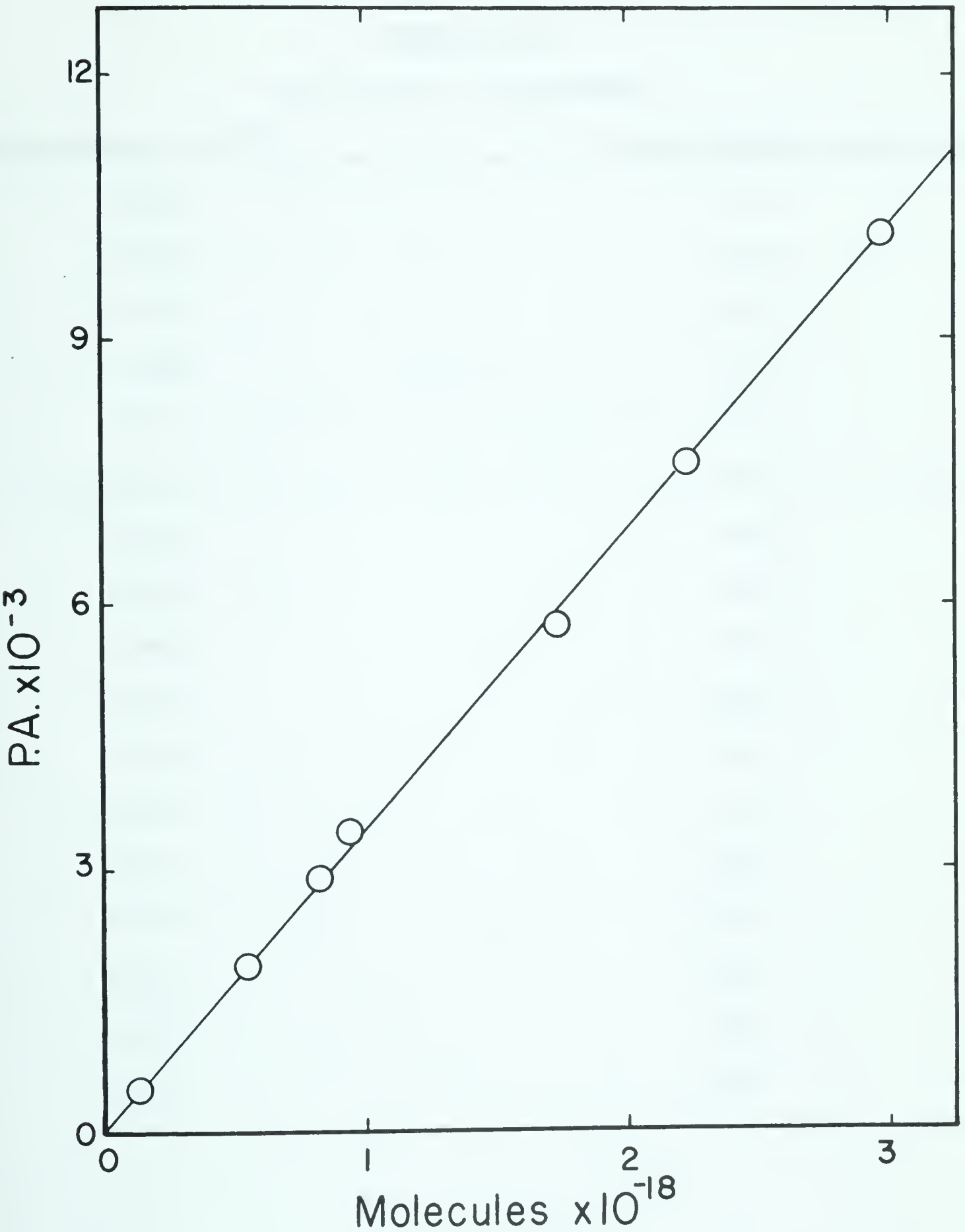

P.A. x10-3
12
9
6
3
0
0
1
2
3
Molecules x10-18

TABLE II 8

Calibration of Hydrogen.

Molecules x 10^{-18}	Peak Height (unit, 1/50")
0.258	6.0
0.416	13.4
0.700	25.2
0.798	31.1
1.26	52.5
1.27	50.5
1.67	83.3
1.89	82.4
2.48	117.
2.51	106.
2.54	109.
2.72	117.
3.07	118.
4.20	177.
5.06	206.
5.99	228.
6.34	245.

TABLE II 9

Calibration of Carbon Monoxide.

Molecules x 10^{18}	Peak Area [unit, $(1/50")^2$]
0.144	493
0.549	1970
0.840	2865
0.952	3400
1.73	5740
2.23	7600
2.98	10250

c. Calibrations of C_5 and C_{10} Products

Solutions of the various liquid products were prepared by weight using cyclopentanone as the solvent. The calibration factors (CF) were determined from expression II-3.

$$CF = \frac{\text{Peak Area of Product/Peak Area of Cyclopentanone}}{\text{Moles of Product/Moles of Cyclopentanone}} \quad \text{(II-3)}$$

For most liquid products the calibration factors were not linear with concentration. The concentrations of the calibration solution approximated those encountered in radiolyzed samples.

Authentic samples were used for all calibrations except that bicyclopentyl-2,2'-dione was the only "dimer" used.

d. Calibrations of Cyclopentanol for Cyclopentanone Samples Containing Benzene

The separation of the cyclopentanol and cyclopentanone peaks was not too satisfactory on either GC column used and was dependent upon the amount of ketone injected. A separate calibration curve for cyclopentanol was therefore determined for each additive concentration. This was accomplished by varying the volume of the cyclopentanol/cyclopentanone solution injected. Five different volumes corresponding to five concentrations of benzene or pentadiene in cyclopentanone were injected from each of the standard solutions prepared and the resulting calibration

factors for the Ucon and Carbowax columns are illustrated in Fig. II 9 and 10 respectively, and the data are summarized in Tables II 10 and II 11.

e. Calibration of 4-Pentenal in the Presence of Benzene

The separation of the GC peaks of 4-pentenal and benzene decreased with increasing benzene concentration. It was therefore necessary to calibrate 4-pentenal in benzene as a function of the volume of the injection as well as the aldehyde concentration. These data are represented graphically in Figs. II 11 and 12 and in tabular form in Tables II 12 and II 13.

FIGURE II 9

Cyclopentanol Calibrations on the Carbowax Column.

A.R. = Area of the Peak/Area of the Cyclopentanone Peak

C.F. = Calibration factor

	Volume injected (µl)
A	26
B	50
C	66
D	80
E	100

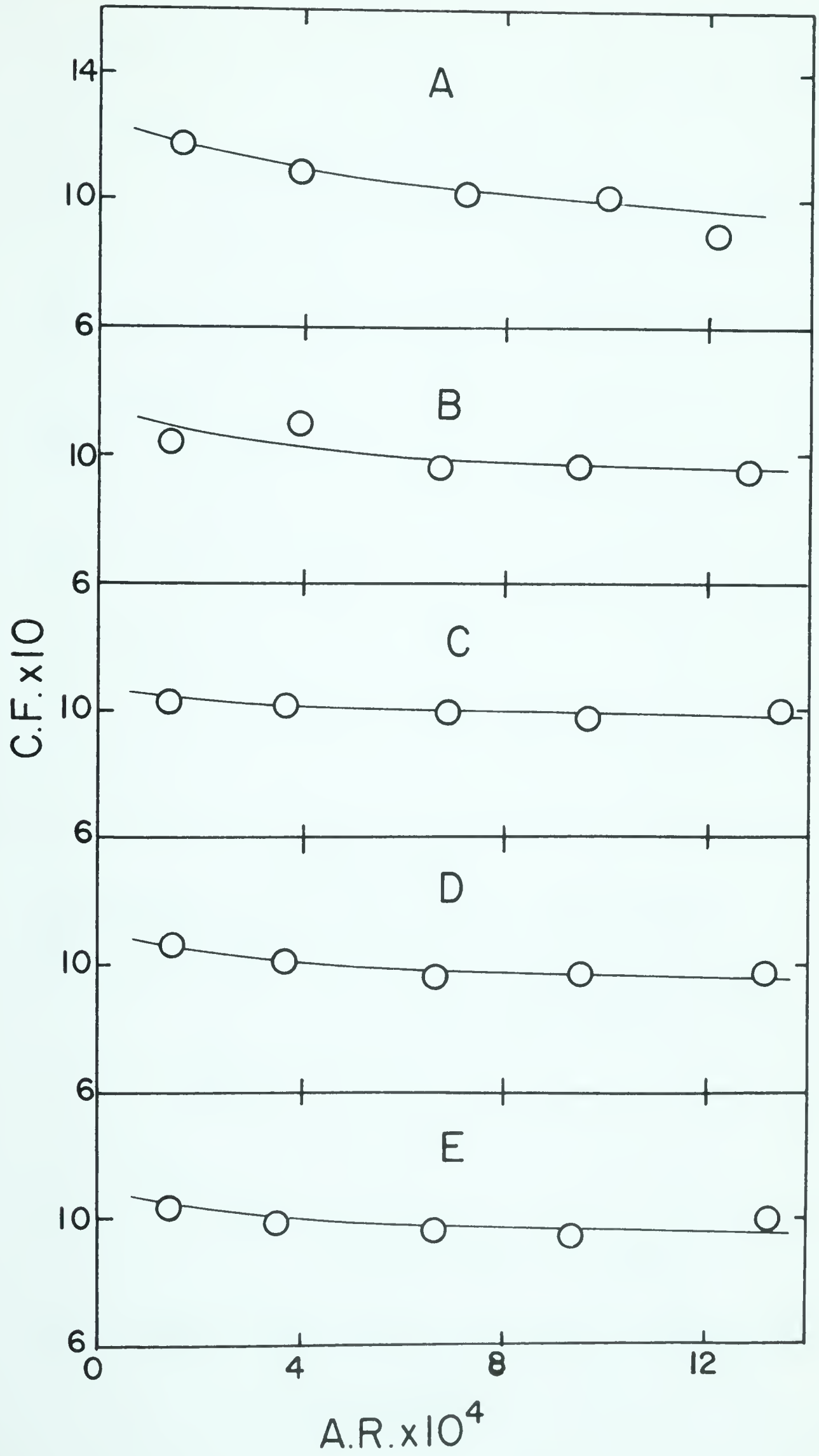

A
B
C
D
E
14
10
6
C.F. x10
0
4
8
12
A.R. x10^4

FIGURE II 10

Cyclopentanol Calibrations on the Ucon Column.

A.R. = Area of the Peak/Area of the Cyclopentanone Peak

C.F. = Calibration factor

	Volume injected (µl)
A	26
B	50
C	66
D	80
E	100

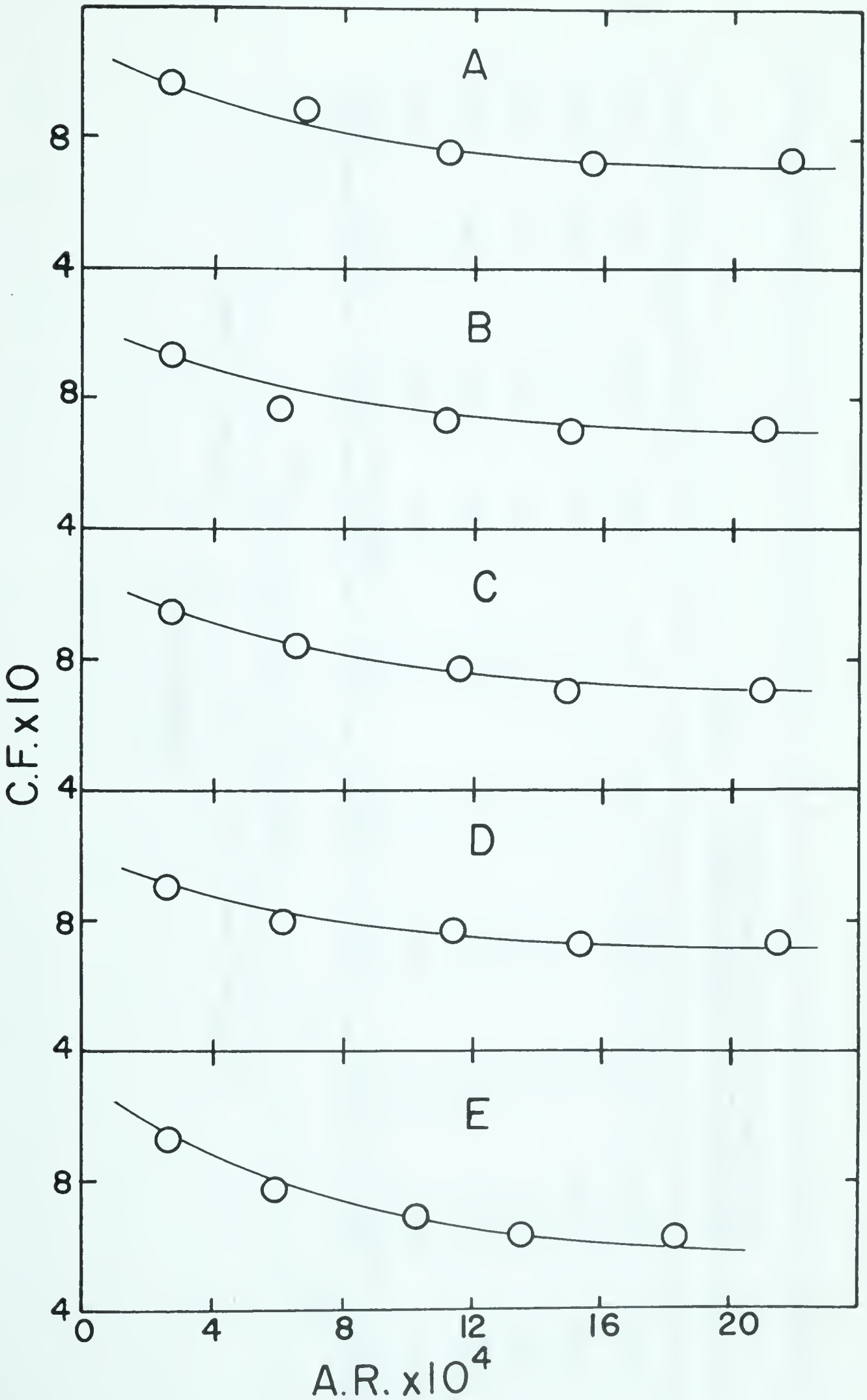

A
B
C
D
E
8
4
C.F. x10
0
4
8
12
16
20
A.R. x10^4

TABLE II 10

Cyclopentanol Calibrations on the Carbowax Column.

Volume of injection (μl)									
100		80		66		50		26	
A.R.*	C.F.	A.R.*	C.F.	A.R.*	C.F.	A.R.*	C.F.	A.R.*	C.F.
13.3	0.99	13.2	0.98	13.5	1.00	12.8	0.95	12.2	0.90
9.31	0.95	9.51	0.97	9.65	0.95	9.45	0.96	9.96	1.01
6.65	0.96	6.62	0.96	6.83	0.99	6.68	0.95	7.15	1.03
3.50	0.98	3.63	1.01	3.62	1.01	3.93	1.10	3.91	1.09
1.35	1.03	1.39	1.06	1.34	1.02	1.36	1.04	1.55	1.18

* A.R. = $\frac{\text{Peak area of cyclopentanol}}{\text{Peak area of cyclopentanone}} \times 10^4$

TABLE II 11

Cyclopentanol Calibrations on the Ucon Column.

Volume of injection (µl)									
100		80		66		50		26	
A.R.*	C.F.	A.R.*	C.F.	A.R.*	C.F.	A.R.*	C.F.	A.R.*	C.F.
18.3	0.62	21.5	0.73	21.0	0.71	21.1	0.71	21.8	0.74
13.5	0.63	15.3	0.72	14.9	0.70	15.0	0.70	15.6	0.73
10.3	0.69	11.4	0.76	11.6	0.77	11.1	0.74	11.2	0.75
5.93	0.77	6.15	0.80	6.56	0.85	5.98	0.77	6.84	0.88
2.63	0.93	2.55	0.90	2.69	0.95	2.67	0.94	2.73	0.97

* $A.R. = \frac{\text{Peak area of cyclopentanol}}{\text{Peak area of cyclopentanone}} \times 10^4$

FIGURE II 11

Calibration of 4-Pentenal in Benzene Solution on the Carbowax Column.

A.R. = Area of the Peak/Area of the Benzene Peak

C.F. = Calibration factor

	Volume injected (µl)
A	18
B	34
C	56
D	68
E	80
F	100

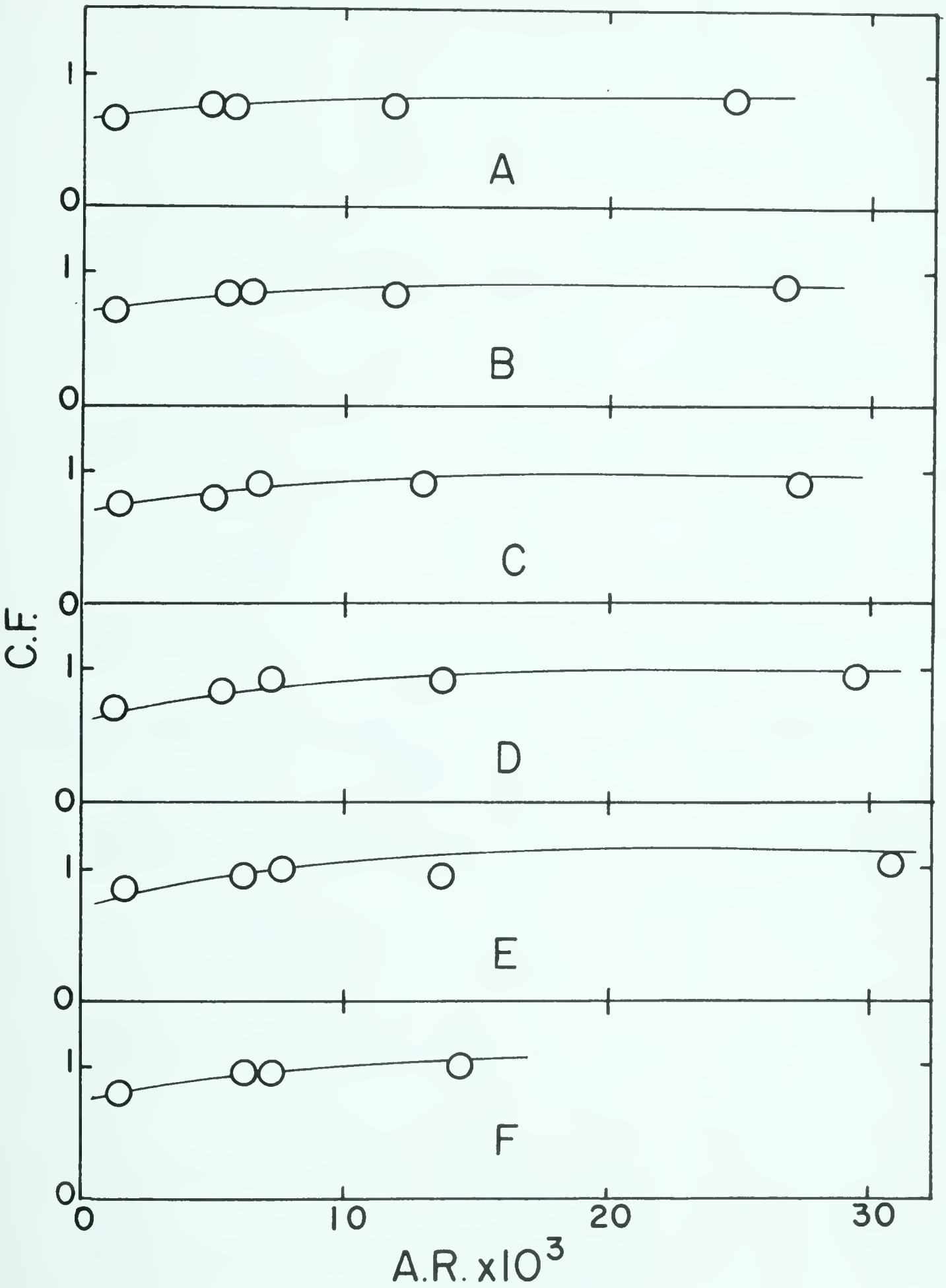

C.F.
1
0
A
B
C
D
E
F
0
10
20
30
A.R. x10^3

FIGURE II 12

Calibration of 4-Pentenal in Benzene Solution on the Ucon Column.

A.R. = Area of the Peak/Area of the Benzene Peak

C.F. = Calibration Factor

	Volume injected (µl)
A	18
B	34
C	56
D	68
E	80
F	100

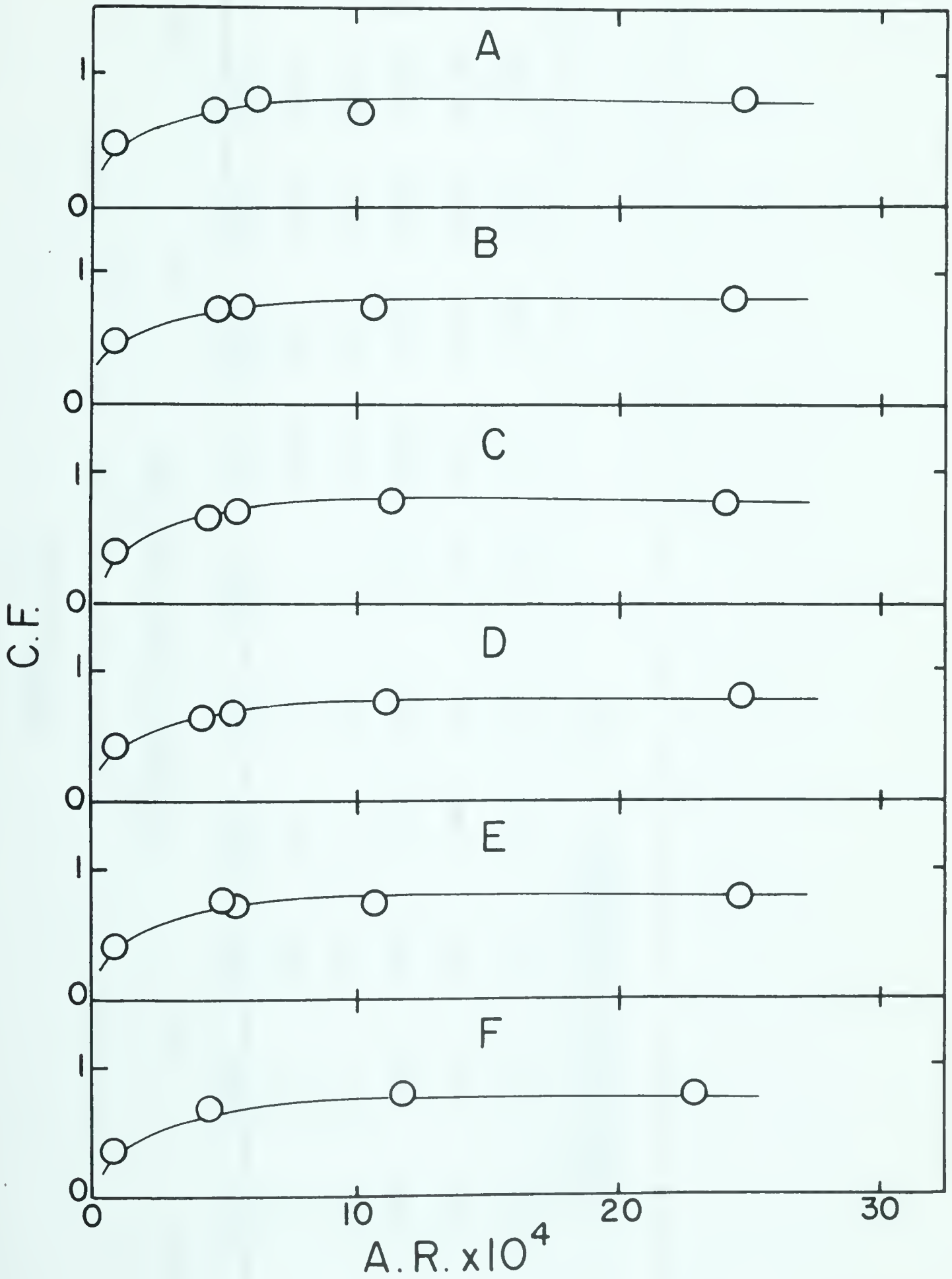

A
B
C
D
E
F
1
0
C.F.
0
10
20
30
A.R. x10^4

TABLE II 12

4-Pentenal Calibrations in Benzene Solutions on the Carbowax Column.

Volume of injection (µl)											
100		80		68		56		34		18	
A.R.*	C.F.	A.R.*	C.F.	A.R.*	C.F.	A.R.*	C.F.	A.R.*	C.F.	A.R.*	C.F.
-	-	30.9	1.02	29.5	0.97	27.3	0.90	26.9	0.89	24.8	0.82
14.5	1.01	13.7	0.95	13.7	0.95	13.0	0.90	12.0	0.83	11.2	0.78
7.34	0.96	7.60	0.99	7.22	0.94	6.83	0.89	6.45	0.84	5.81	0.76
6.24	0.96	6.11	0.94	5.44	0.84	5.10	0.79	5.59	0.86	4.93	0.76
1.53	0.80	1.65	0.86	1.38	0.72	1.48	0.77	1.34	0.70	1.28	0.67

* A.R. = $\frac{\text{Peak area of 4-Pentenal}}{\text{Peak area of benzene}} \times 10^4$

TABLE II 13

4-Pentenal Calibrations in Benzene Solutions on the Ucon Column.

Volume of injection (µl)											
100		80		68		56		34		18	
A.R.*	C.F.	A.R.*	C.F.	A.R.*	C.F.	A.R.*	C.F.	A.R.*	C.F.	A.R.*	C.F.
23.0	0.76	24.6	0.81	24.7	0.81	24.1	0.79	24.5	0.81	24.9	0.82
11.8	0.81	10.7	0.74	11.1	0.77	11.4	0.79	10.7	0.74	10.2	0.71
-	-	5.41	0.71	5.26	0.69	5.46	0.71	5.65	0.74	6.27	0.82
4.55	0.70	4.96	0.76	4.19	0.65	4.44	0.68	4.75	0.73	4.67	0.72
0.73	0.38	0.80	0.42	0.82	0.43	0.77	0.40	0.93	0.49	0.90	0.47

* $A.R. = \frac{\text{Peak area of 4-pentenal}}{\text{Peak area of benzene}} \times 10^4$

III. RESULTS

A. Products Arising from C-H Bond Cleavage

1. Radiolysis of Pure Cyclopentanone

The products resulting from C-H bond rupture which were identified in the present study consisted of hydrogen, cyclopentanol, 2-cyclopentenone, and bicyclopentyl-2,2'-dione (BCD). It should be noted, however, that the presence of 3-cyclopentenone among the products could not be proved or disproved on the basis of this study.

Several GC peaks which had retention times quite close to that of BCD were observed but no attempt was made to identify the individual compounds because of their small yields. The yield of total "dimers" (ie. all C_{10} products) was calculated using the calibration factor of BCD. In addition to these C_5 and C_{10} products, a large quantity of chloroform soluble polymer was also formed. It is possible that this polymer contained carbon chains as well as ketone rings, but it will be considered with the above products.

The straight lines in the figures which correlate the product yields with the irradiation doses for the products from pure cyclopentanone were calculated by the least squares method. The dose rate range was 2 - 11 (10^{18} eV/ml hr).

a. Hydrogen

The yield of hydrogen as a function of the absorbed dose is presented in Fig. III 1A and in Table III 1. The initial yield [G value extrapolated to zero dose, $G_i(H_2)$], is 0.78, and the yield decreases slightly with increasing dose.

b. Cyclopentanol

The initial yield of cyclopentanol is 0.84. The dose-dependence of the alcohol yield is shown graphically in Fig. III 1B, each point of which represents the average of the values obtained from the Ucon and Carbowax columns. The data are also given in Table III 2. Despite the scatter, a definite decrease in the alcohol yield with increasing dose is shown.

c. Cyclopentenone

2-Cyclopentenone, which has an initial yield of 0.09, also shows a decreased yield with increasing dose (see Fig. III 1B and Table III 3).

d. Dimers

The yields of total dimer and BCD as functions of the absorbed dose are illustrated in Fig. III 2A. The total dimer yields from both the Apiezon L and Silicone grease columns are included in this figure. For reasons of clarity, only the average values of the BCD yields from these columns are presented in this figure. These data are listed in Table III 4. The initial yields of

FIGURE III 1

Yields of Hydrogen, Cyclopentanol, and Cyclopentenone as Functions of Dose

A: Hydrogen

B: ○ Cyclopentanol

● Cyclopentenone

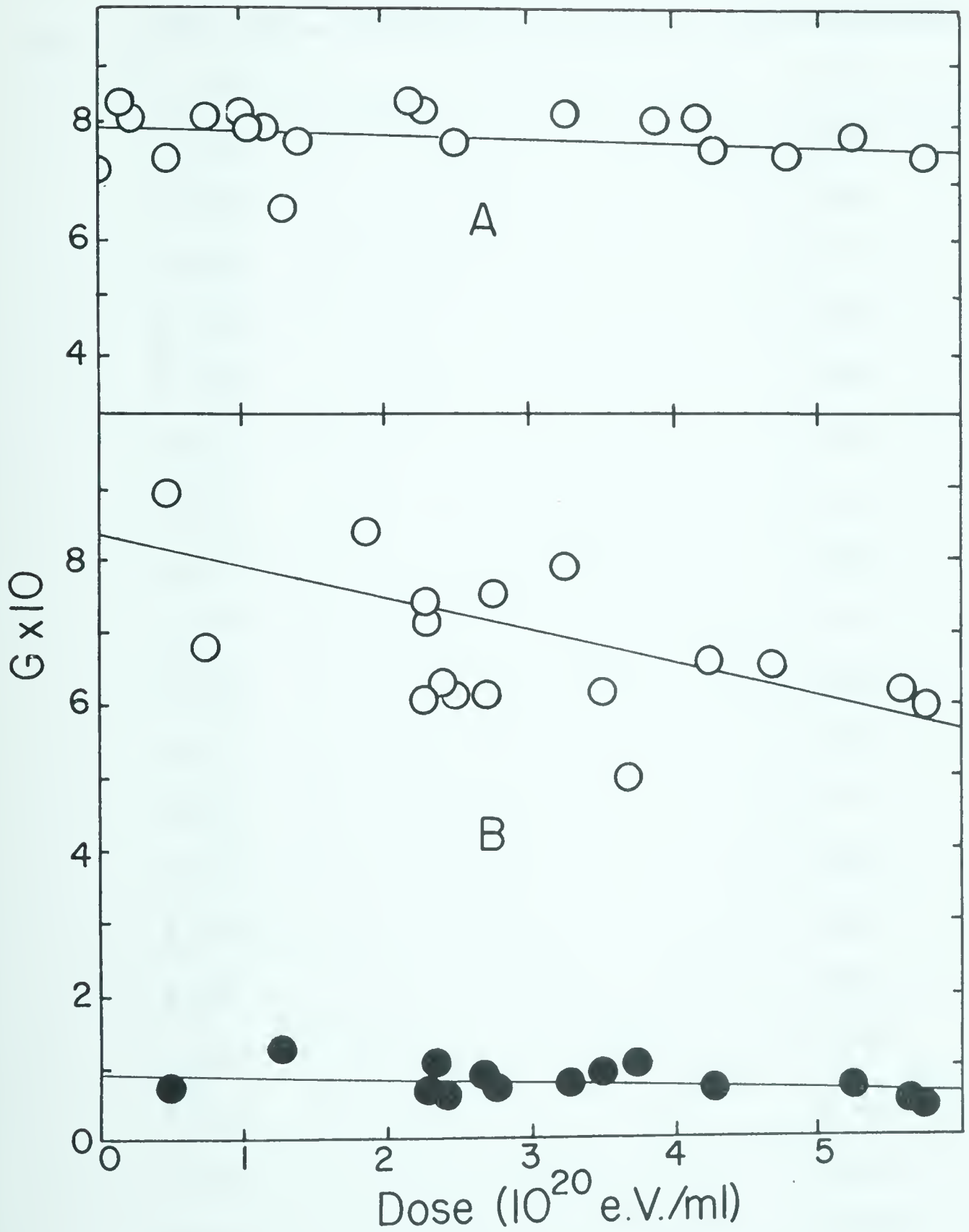

G x 10
8
6
4
A
8
6
4
2
0
B
0
1
2
3
4
5
Dose (10^20 e.V./ml)

TABLE III 1

Hydrogen Yields from Cyclopentanone, as a Function of Dose.

Dose rate range = 2 - 11 (10^{18} eV/ml hr)

Dose (10^{20} eV/ml)	G (Hydrogen)
0.0505	0.72
0.150	0.84
0.250	0.81
0.496	0.74
0.754	0.81
0.982	0.82
1.04	0.79
1.15	0.79
1.30	0.65
1.39	0.77
2.20	0.84
2.25	0.82
2.46	0.77
3.25	0.82
3.85	0.81
4.15	0.82
4.25	0.74
4.75	0.74
5.25	0.78
5.75	0.74

TABLE III 2

Cyclopentanol Yields from Cyclopentanone, as a Function of Dose.

Dose rate range = 2-11 (10^{18} eV/ml hr)

Dose (10^{20} eV/ml)	G (Cyclopentanol) *
0.508	0.89
0.751	0.68
1.85	0.84
2.25	0.61
2.28	0.74
2.32	0.71
2.45	0.63
2.50	0.61
2.75	0.61
2.78	0.75
3.25	0.79
3.50	0.62
3.69	0.50
4.27	0.66
4.70	0.65
5.64	0.62
5.75	0.60

* Average value obtained from Carbowax and Ucon columns.

TABLE III 3

Cyclopentenone Yields from Cyclopentanone, as a Function of Dose.

Dose rate range = 2 - 11 (10^{18} eV/ml hr)

Dose (10^{20} eV/ml)	G (Cyclopentenone) *
0.508	0.075
1.27	0.124
2.25	0.069
2.32	0.104
2.45	0.060
2.66	0.090
2.78	0.065
3.25	0.075
3.50	0.087
3.75	0.100
4.27	0.074
5.25	0.072
5.64	0.056
5.75	0.044

* Separable from cyclopentanol on the Carbowax column only.

FIGURE III 2

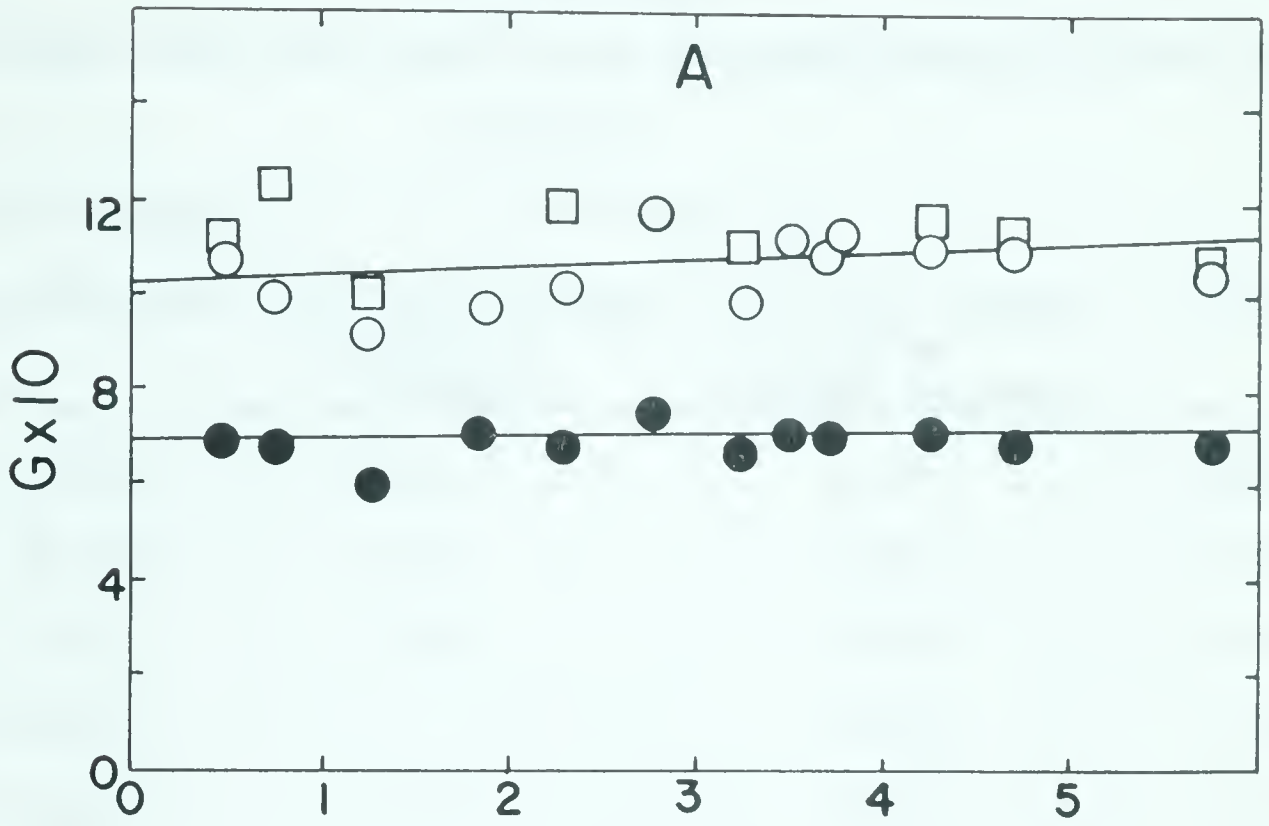
Yields of Dimers and Polymers as Functions of Dose

A: □ total dimer (Apiezon L column)

○ total dimer (Silicone grease column)

● BCD (average of Apiezon L and Silicone grease columns)

B: Polymer yield (excluding dimer), expressed in cyclopentanone units. ○ , samples sent for microanalysis.


A
G x 10
12
8
4
0
0
1
2
3
4
5

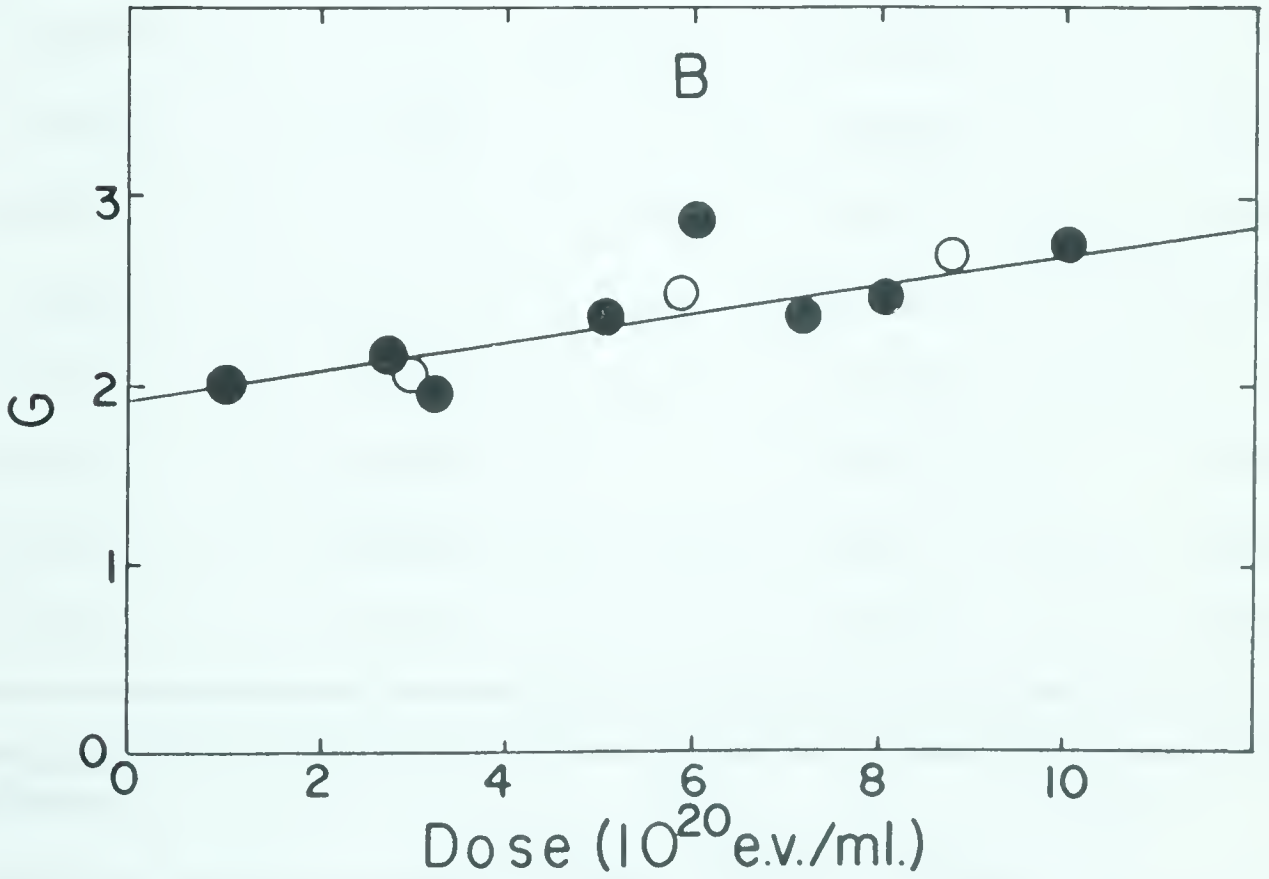

B
G
3
2
1
0
0
2
4
6
8
10
Dose (10^{20} e.v./ml.)

TABLE III 4

Total Dimer and BCD Yields from Cyclopentanone as Functions of Dose.

Dose rate range = 2 - 11 (10^{18} eV/ml hr)

Dose (10^{20}eV/ml)	G (Total dimer) (Apiezon L column)	G (Total dimer) (Silicone grease column)	G (BCD)*
0.508	1.12	1.09	0.70
0.751	1.24	1.00	0.69
1.27	1.01	0.93	0.60
1.85	-	0.98	0.70**
2.32	1.19	1.02	0.68
2.78	-	1.18	0.75**
3.25	1.11	0.99	0.67
3.50	-	1.13	0.72**
3.69	-	1.10	0.72**
3.75	-	1.14	- **
4.27	1.16	1.11	0.72
4.70	1.15	1.11	0.69
5.75	1.07	1.06	0.69

* Average value obtained from Apiezon L and Silicone grease columns.

** Analyzed only on the Silicone grease column.

BCD and total dimer are 0.69 and 1.0, respectively. The blanks in the second column of Table III 4 resulted from the analysis of these samples on the Silicone grease column only.

e. Polymer

The yield of chloroform soluble polymer (excluding dimer) as a function of the absorbed dose is given in Table III 5 and is illustrated in Fig. III 2B. The polymer yields are reported in units of monomer reacted to form polymer. The initial yield of polymer is 1.9. Double determinations of carbon and hydrogen content, the average molecular weight, and the iodine number, were obtained for each of three samples. These samples are differentiated in Fig. III 2B. No dose dependence of the polymer composition or molecular weight was observed and the average values are therefore presented in Table III 6 together with those calculated for cyclopentanone. The values for the polymer in this table have been corrected for the predetermined content of C_5 and C_{10} compounds in the material analyzed (1% monomer, 40% dimer, and 59% polymer) as well as for the residual chloroform. An average of one olefinic bond for every eight monomer units incorporated into the polymer was also found. The average molecular weight of the polymer (388) lies between those of the "tetramer" (336) and the

TABLE III 5

Yields of Chloroform Soluble Polymer (excluding dimer) from Cyclopentanone, as a Function of Dose.

Dose rate range = 2 - 11 (10^{18} eV/ml hr)

Dose (10^{20} eV/ml)	G (Polymer) *
1.06	2.01
2.69	2.14
3.00	2.04
3.25	1.95
5.05	2.33
5.82	2.47
6.00	2.86
7.14	2.32
8.10	2.45
8.80	2.68
9.98	2.72

* In units of monomer reacted to form polymer.

TABLE III 6

Microanalysis of Polymer from Cyclopentanone.

	1	2
% C	71.4	72.6
% H	9.6	9.4
% O	19.0	18.0[a]
MW	84.1	388.[b]

1: Values calculated for cyclopentanone.

2: Average values obtained for polymer (excluding dimer) from three samples.

a: Obtained by difference.

b: Obtained by Rast method.

"pentamer" (420).

A summary of the initial G values of these products is presented in Table III 7.

2. Cyclopentanone Solutions

When considering the effects of additives on the yield of a product, P, a comparison between the observed yield, G(P), and the expected yield, $G_{ex}(P)$, may be discussed. $G_{ex}(P)$ is the yield which would be observed if the contribution of each component of a binary solution to the observed yield of the product, were directly proportional to the electron fraction of the component in the sample. The values of G_{ex} are shown as dashed lines in Figs. III 3, III 4, and III 5 and in all of these figures G(P) is less than $G_{ex}(P)$.

Two ml samples containing benzene or 1,3-pentadiene or solutions of these compound with cyclopentanone received doses of $8.0 \pm 0.1 \times 10^{-4}$ eV/e^- (about 2×10^{20} eV/ml). This dose was used to insure that the cyclopentanone in each sample absorbed the same amount of energy.

a. Hydrogen

The reduction in the hydrogen yield resulting from the addition of 1,3-pentadiene (Fig. III 3A) is much more marked at low additive concentration than that caused by benzene (Fig. III 3B). Fig. III 3B also indicates a lack

TABLE III 7

The Initial Yields of Products Arising from the C-H Bond Cleavage of Cyclopentanone.

Product	G_i*
Hydrogen	0.78 ± 0.06
Cyclopentenone	0.09 ± 0.04
Cyclopentanol	0.84 ± 0.15
Total dimer	1.0 ± 0.1
BCD	0.69 ± 0.05
Polymer **	1.9 ± 0.3

* G values extrapolated to zero dose.

** Excluding dimer and reported in units of monomer reacted to form polymer.

FIGURE III 3

Hydrogen Inhibition

ϵ_s = electron fraction of solute

Dashed lines represent G_{ex}

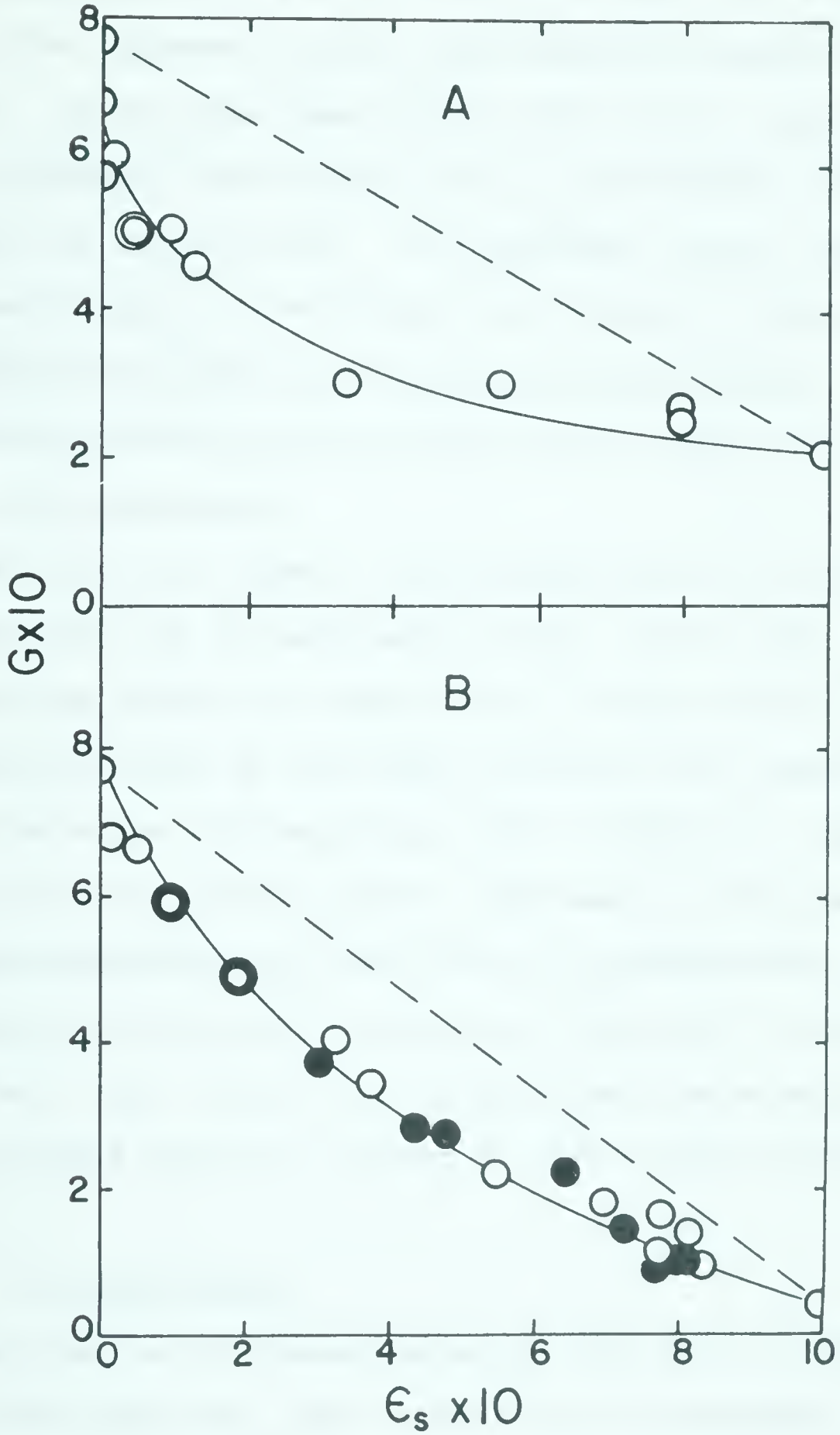
Dose = 8.0 ± 0.1 (10^{-4}eV/e$^-$), about 2 x 10^{20} eV/ml.

A: 1,3-Pentadiene solutions, dose rate = 1.73 ± 0.02 (10^{-4} eV/e$^-$hr)

B: Benzene solutions

○ Dose rate = 1.73 ± 0.02 (10^{-4} eV/e$^-$ hr)

● Dose rate = 6.6 ± 0.3 (10^{-6} eV/e$^-$ hr)


A
B
G x 10
ϵ_s x 10
0
2
4
6
8
10

of dose dependence (17.3×10^{-5} eV/e^- hr and 0.66×10^{-5} eV/e^- hr) for hydrogen yields from benzene/cyclopentanone solutions. At the dose used (8.0×10^{-4} eV/e^-) the G values of hydrogen from benzene and 1,3-pentadiene were 0.038 and 0.20 respectively. The hydrogen yields from samples containing 1,3-pentadiene are listed in Table III 8, while the yields from benzene/cyclopentanone samples are differentiated by dose rate in Table III 9.

b. Cyclopentanol

The effect of added 1,3-pentadiene on the yield of cyclopentanol is illustrated in Figs. III 4A and III 4B and the yields are summarized in Table III 10. An electron fraction of the diene of about 0.01 reduces the yield to below the detection limit ($G < 0.1$). The addition of benzene also causes a decrease in the alcohol yield. The dependence of the yield of cyclopentanol on the benzene concentration is shown in Table III 11 and Fig. III 4B. Fig. III 4B also illustrates the relative effects of added diene or benzene on the G value of the alcohol.

c. Cyclopentenone

The yield of cyclopentenone was only 0.07 at the dose used for mixtures, and it could not be detected as a product from any of these solutions.

d. Destruction of 1,3-Pentadiene

The consumption of 1,3-pentadiene as a function of

TABLE III 8

Hydrogen Yields from Cyclopentanone/1,3-Pentadiene Solutions.

Dose rate = 1.73 ± 0.02 (10^{-4} eV/e^- hr)

Dose = 8.0 ± 0.1 (10^{-4} eV/e^-), about 2 x 10^{20} eV/ml.

Electron Fraction 1,3-Pentadiene	G (Hydrogen)
0.0043	0.68
0.0109	0.58
0.0206	0.61
0.0516	0.50
0.0529	0.50
0.100	0.51
0.131	0.46
0.344	0.30
0.548	0.30
0.795	0.27
0.797	0.25
1.000	0.20
1.000	0.20

TABLE III 9

Hydrogen Yields from Cyclopentanone/Benzene Solutions.

Dose = 8.0 ± 0.1 (10^{-4} eV/e$^-$), about 2 x 10^{20} eV/ml

Electron Fraction Benzene	G (Hydrogen) A	B
0.0208	0.68	-
0.0554	0.66	-
0.100	-	0.58
0.101	0.58	-
0.193	-	0.48
0.194	0.48	-
0.313	-	0.37
0.325	0.40	-
0.377	0.34	-
0.437	-	0.28
0.485	-	0.27
0.555	0.22	-
0.647	-	0.22
0.698	0.18	-
0.732	-	0.14
0.778	0.16	-
0.784	0.11	-
0.785	-	0.09
0.801	-	0.10
0.823	0.13	-

Table III 9, continued.

Electron Fraction Benzene	G (Hydrogen) A	B
0.826	-	0.10
0.842	0.09	-
1.000	0.039	-
1.000	-	0.037

A: Dose rate = 17.3 $\pm$ 0.2 (10^{-5} eV/e^- hr)

B: Dose rate = 0.66 $\pm$ 0.03 (10^{-5} eV/e^- hr)

FIGURE III 4

Cyclopentanol Inhibition.

ϵ_s = electron fraction of solute

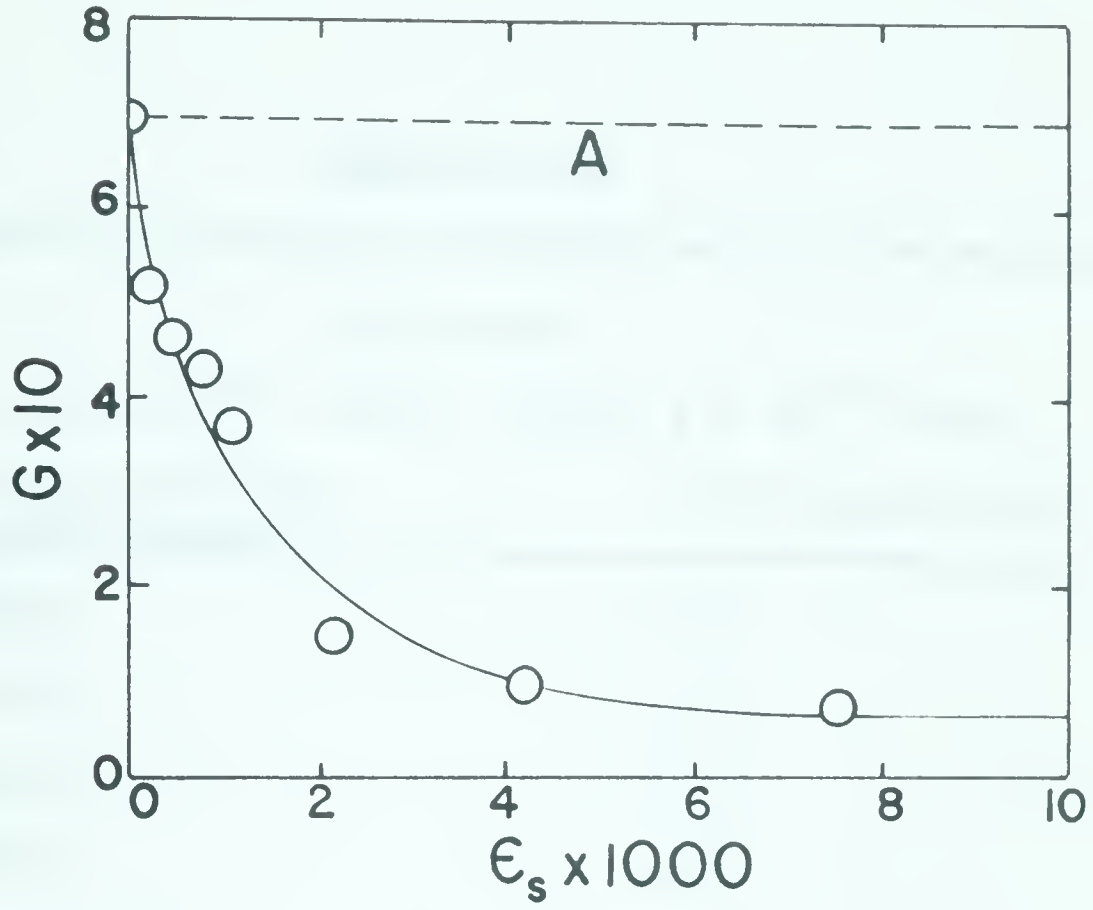
Dashed lines refer to G_{ex}

Dose = 8.0 $\pm$ 0.1 (10^{-4} eV/e^-), about 2 x 10^{20} eV/ml.

A: 1,3-Pentadiene solutions

B: O 1,3-Pentadiene solutions

△ Benzene solutions


A
G x 10
ϵ_s x 1000
0
2
4
6
8
10

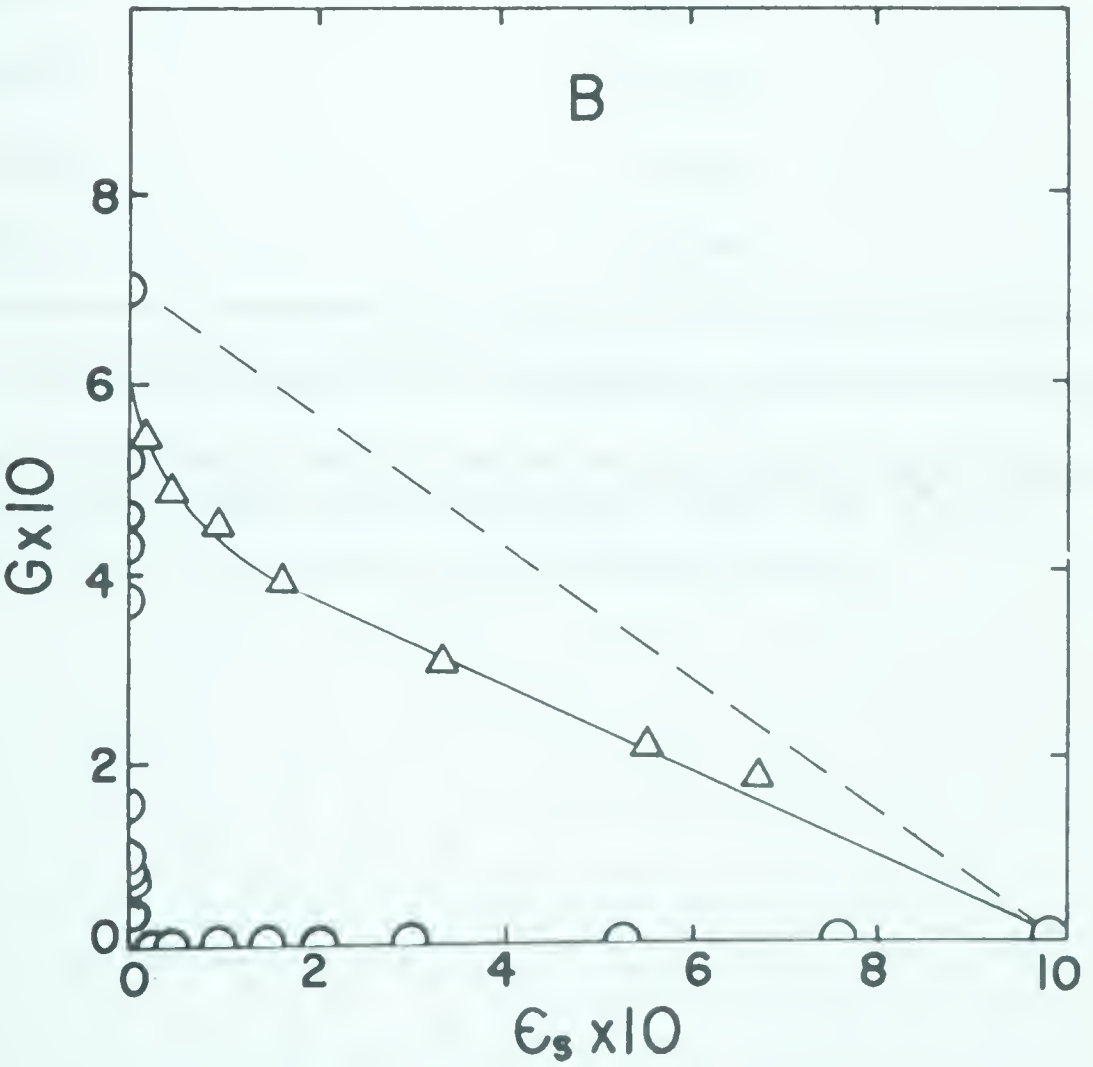

B
G x 10
ϵ_s x 10
0
2
4
6
8
10

TABLE III 10

Cyclopentanol Yields from Cyclopentanone/1,3-Pentadiene Solutions.

Dose = 8.0 ± 0.1 (10^{-4} eV/e$^-$), about 2 x 10^{20} eV/ml

Electron Fraction 1,3-Pentadiene	G (Cyclopentanol) *
0.00027	0.52
0.00052	0.46
0.00081	0.43
0.00107	0.37
0.00215	0.15
0.00425	0.10
0.00758	0.08
0.0111	0.0**

* Average value obtained from Carbowax and Ucon columns.

** Yields of cyclopentanol from more concentrated diene solutions were below the detection limit ($G < 0.1$).

TABLE III 11

Cyclopentanol Yields from Cyclopentanone/Benzene Solutions.

Dose = 8.0 ± 0.1 (10^{-4} eV/e^-), about 2 x 10^{20} eV/ml

Electron Fraction Benzene	G (Cyclopentanol) *
0.0203	0.54
0.0554	0.48
0.0945	0.45
0.177	0.39
0.343	0.30
0.561	0.22
0.682	0.18

* Average value obtained from Carbowax and Ucon columns.

the concentration of the diene is given in Fig. III 5A and the data used in this figure are recorded in Table III 12. The first three points are below the maximum G value of 4.3 $\pm$ 0.3 due to a depletion of the diene during radiolysis, as indicated by the data in this table.

e. Dimers

A very rapid decrease in the yield of the cyclopentanone dimers by 1,3-pentadiene is shown by the data in Table III 13 which are plotted in Fig. III 5B and III 5C. The yield of these dimers is reduced to below the detection limit ($G < 0.05$) by an electron fraction of the diene of about 0.01. The much less pronouced effect of added benzene on the yield of the ketone dimers is shown in Fig. III 5C. The values from which this graph was constructed are listed in Table III 14.

Analytical conditions were such that the GC peaks of the "cross dimers" (i.e. dimers which consist of one ketone and one diene unit) were not sufficiently separated from the pure diene dimers to allow them to be measured separately.

f. Polymer

The yields of chloroform soluble polymer from samples of cyclopentanone containing varying amounts of 1,3-pentadiene are presented in Table III 15 and in Fig.

FIGURE III 5

Yields of Ketone Dimers from Solutions and Rate of Disappearance of 1,3-Pentadiene

ϵ_s = electron fraction of solute

Dashed line refers to G_{ex}

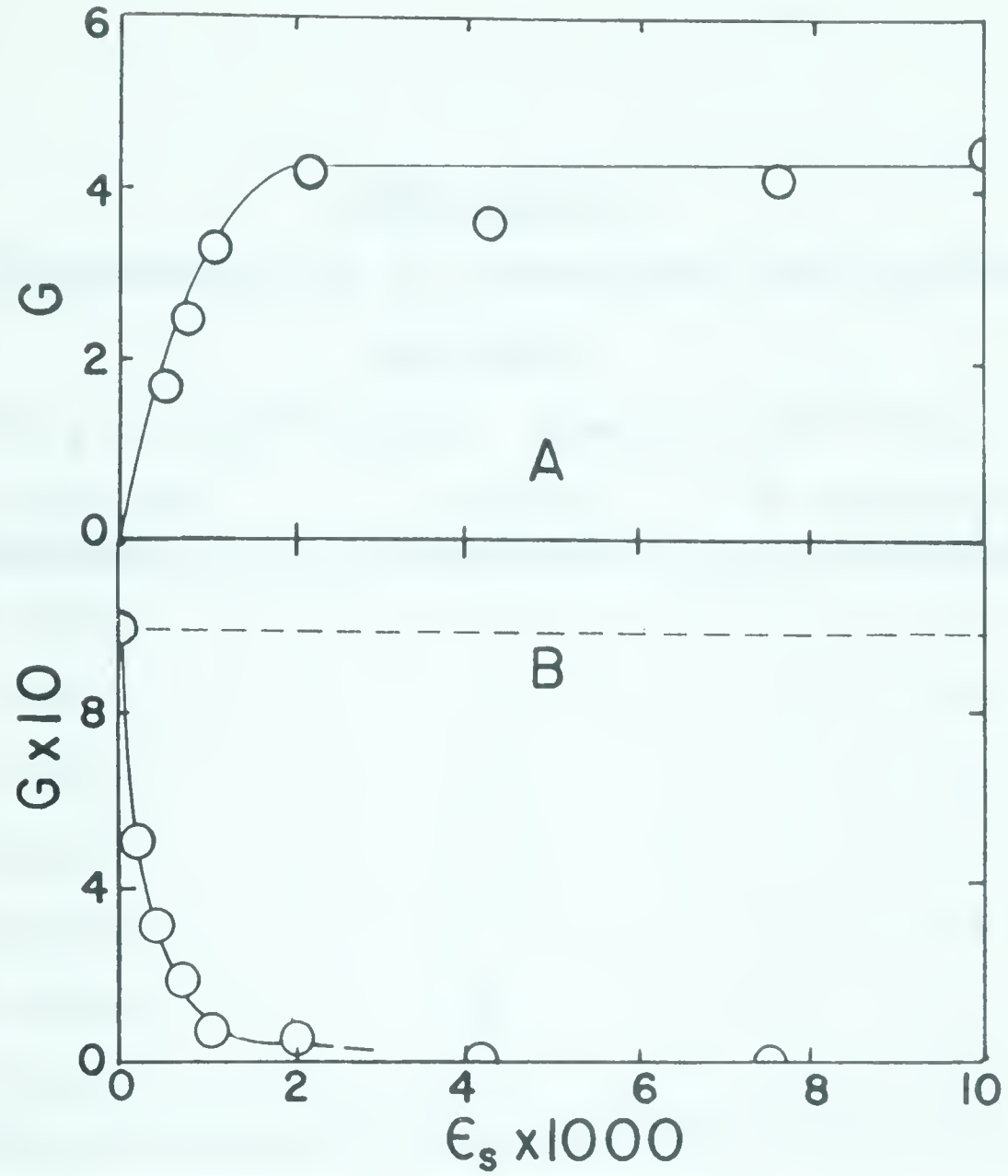
Dose = 8.0 $\pm$ 0.1 (10^{-4} eV/e^-), about 2 x 10^{20} eV/ml.

A: Disappearance of 1,3-pentadiene

B: Yields of ketone dimers from pentadiene solutions.

C: ○ Ketone dimers from benzene solutions.

● Ketone dimers from pentadiene solutions.


G
A
B
G x 10
ϵ_s x 1000

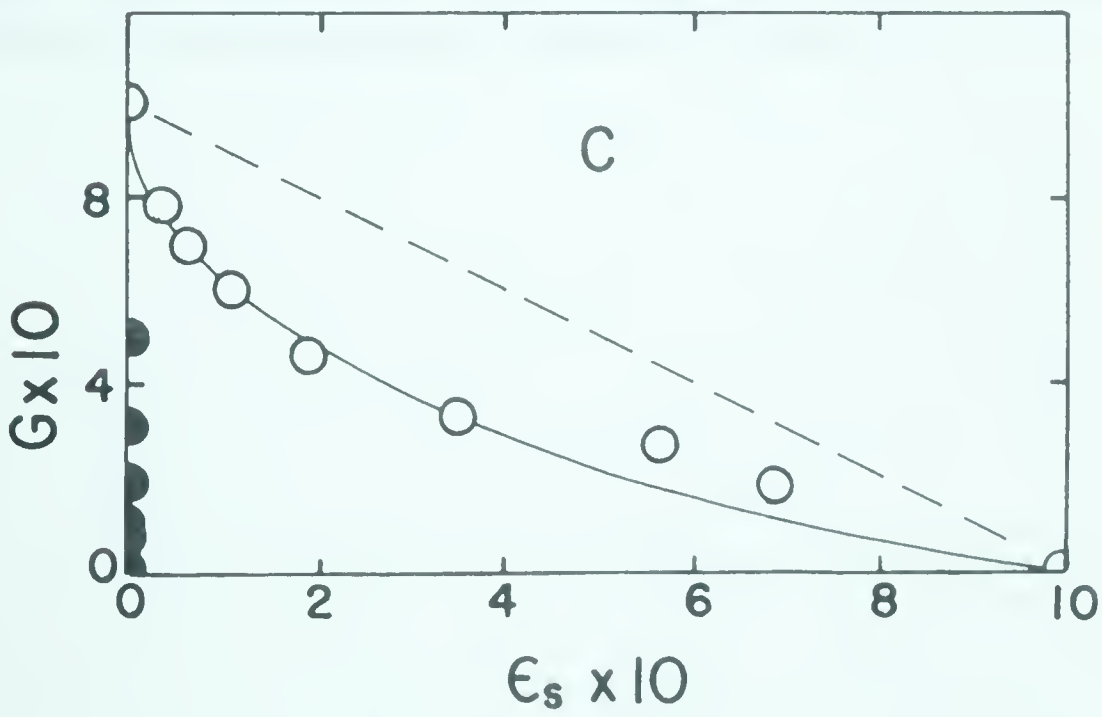

C
G x 10
ϵ_s x 10

TABLE III 12

Rate of Disappearance of 1,3-Pentadiene from Cyclopentanone Solutions.

Dose = 8.0 ± 0.1 (10^{-4} eV/e^-), about 2 x 10^{20} eV/ml

Electron Fraction 1,3-Pentadiene	% Diene Remaining	G (Consumption of the diene) *
0.00052	0	1.7
0.00081	5	2.5
0.00107	6	3.3
0.00215	39	4.2
0.00425	74	3.6
0.00758	84	4.1
0.0111	87	4.7

* Average value obtained from Carbowax and Ucon columns.

TABLE III 13

Yields of Ketone Dimers from Cyclopentanone/1,3-Pentadiene Solutions.

Dose = 8.0 ± 0.1 (10^{-4} eV/e$^-$), about 2 x 10^{20} eV/ml

Electron Fraction 1,3-Pentadiene	G (Total Ketone Dimers) *
0.00027	0.50
0.00052	0.31
0.00081	0.18
0.00107	0.07
0.00215	0.05
0.00425	0.0**

* Average value obtained from Silicone grease and Apiezon L columns.

** Yields of dimers from more concentrated diene solutions were below the detection limit ($G < 0.05$).

TABLE III 14

Yields of Ketone Dimers from Cyclopentanone/Benzene Solutions.

Dose = 8.0 ± 0.1 (10^{-4} eV/e$^-$), about 2 x 10^{20} eV/ml

Electron Fraction Benzene	G (Total Ketone Dimers) *
0.0203	0.77
0.0554	0.70
0.0945	0.60
0.177	0.46
0.343	0.33
0.561	0.27
0.682	0.18

* Average value obtained from Silicone grease and Apiezon L columns.

FIGURE III 6

Polymer Yield from Pentadiene Solutions.

ϵ_s = electron fraction of solute

The yield is reported in C_5 units.

Dose = 12 ± 1 (10^{-4} eV/e^-)

● Polymer yield from pure cyclopentanone at the dose used for the diene solutions.

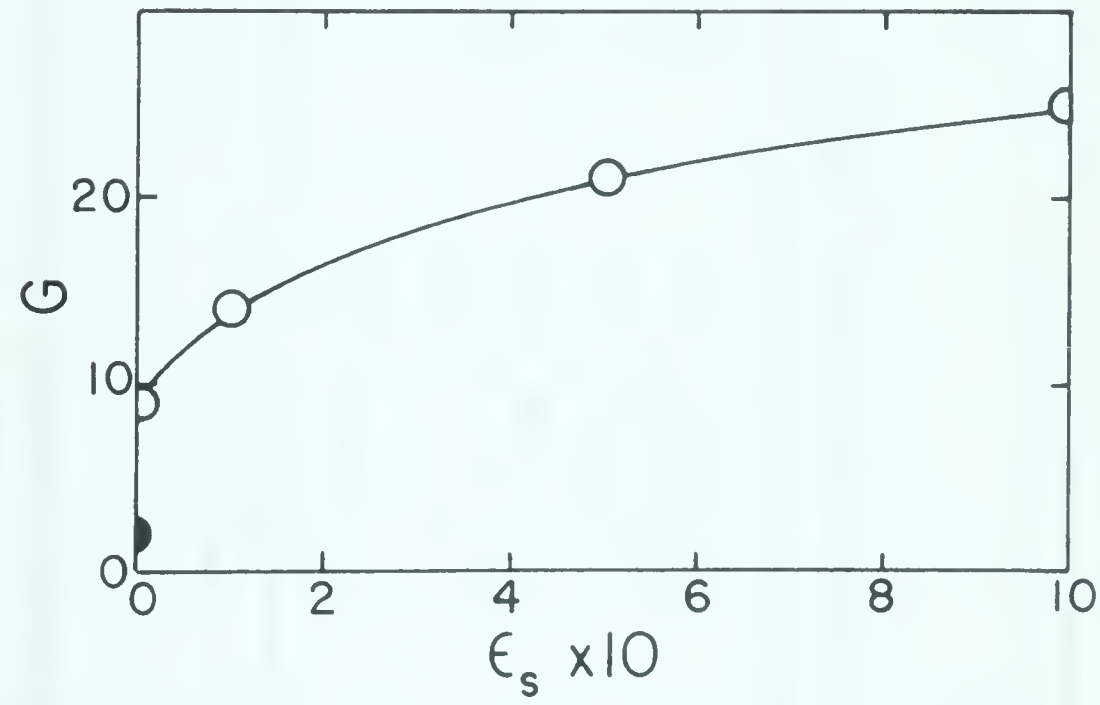

G
20
10
0
0
2
4
6
8
10
ϵ_s x10

TABLE III 15

Polymer Yields from Cyclopentanone/1,3-Pentadiene Solutions.

Dose = 12 ± 1 (10^{-4} eV/e$^-$)

Electron Fraction 1,3-Pentadiene	Weight of Polymer (mg)	Empirical Formula[a]	G (Polymer)[b]
0	9.4	$C_{5.0}H_{7.7}O_{0.94}$	2.3
0.0030	36.5[c]	$C_{5.0}H_{7.9}O_{0.55}$	9
0.100	55.2	$C_{5.0}H_{7.8}O_{0.39}$	14
0.500	82.0[c]	$C_{5.0}H_{7.8}O_{0.34}$	21
1.000	89.0	$C_{5.0}H_{8.0}O_{0.07}$	25

a: Microanalyses obtained from Pascher and Pascher (1964).

b: Reported in C_5 units.

c: Average of two determinations.

III 6. Also included in this figure and table is the yield of polymer obtained from a sample of pure cyclopentanone at the same dose used for the samples containing pentadiene (12×10^{-4} eV/e$^-$).

The empirical formulas given in Table III 15 were calculated from the microanalyses obtained for the polymer from each of these samples (Pascher and Pascher, 1964). Values obtained from the microanalyses of two of these samples (0.003 electron fraction pentadiene) are also presented in column B of Table III 16. The data in both of these tables have been corrected for the predetermined content of C_5 and C_{10} compounds as well as for the residual chloroform content of the samples analyzed.

Using the G values for the consumption of the diene given above (4.3 ± 0.3), and the weight of the polymer produced, an average G value for the rate of disappearance of cyclopentanone into polymer for these samples was found to be 4.8 ± 0.6. Thus this polymer contained an approximate ratio of 1:1 cyclopentanone : pentadiene units.

B. Products Arising from C-C Bond Cleavage

1. Radiolysis of Pure Cyclopentanone

a. Major Products

The major products ($G > 0.1$) resulting from the radiation induced C-C bond cleavage of cyclopentanone are

TABLE III 16

Analysis of Polymer from Cyclopentanone/1,3-Pentadiene Solutions.

	A	B	C	D
% Carbon	71.4	78.3	79.4	88.2
% Hydrogen	9.6	10.2	10.0	11.8
% Oxygen	19.0	11.5	10.6	0
Molecular weight	84.1	306. *	303.	68.2
Moles of Olefinic bonds/100 g	0	0.72**	0.66	2.9

A: Values required for cyclopentanone.

B: Average of two samples containing 0.003 electron fraction diene. Dose = 3.2×10^{20} eV/ml.

C: Values required for $C_{20}H_{30}O_2$.

D: Values required for pentadiene.

* Obtained by the Rast method.

** Based on Iodine number.

carbon monoxide, ethylene, and 4-pentenal. The yields of the gaseous products were investigated over the dose region of 0.05 - 5.75 x 10^{20} eV/ml. The yield of 4-pentenal was studied over the region from 0.5 - 5.75 x 10^{20} eV/ml. The dose-yield lines drawn in Fig. III 7 were calculated by the least squares method.

(1) Carbon monoxide

The dose-yield behavior of carbon monoxide is presented in Fig. III 7A and Table III 17. The initial yield $\left[G_i(CO)\right]$ is 0.68, and the yield is unaffected by increasing dose.

(2) Ethylene

G_i(Ethylene) is 0.80, and the lack of dose dependence of the yield is shown in Fig. III 7B and Table III 18.

(3) 4-Pentenal

The initial yield of 4-pentenal is 0.84 and the yield decreases with increasing dose as shown by the data in Table III 19 which are plotted in Fig. III 7C.

The initial yields of these three products, together with the limits which were visually estimated from the appropriate graphs, are summarized in Table III 20.

b. Minor Products

Several minor products ($G < 0.1$) were found in the present study. The yields of ethane, acetylene, propylene, n-butane, methylcyclopropane, 1-butene, and cyclobutane as functions of the absorbed dose are given in Fig. III 8.

FIGURE III 7

Yields of Carbon Monoxide, Ethylene and 4-Pentenal as Functions of Dose.

A: Carbon monoxide

B: Ethylene

C: 4-Pentenal

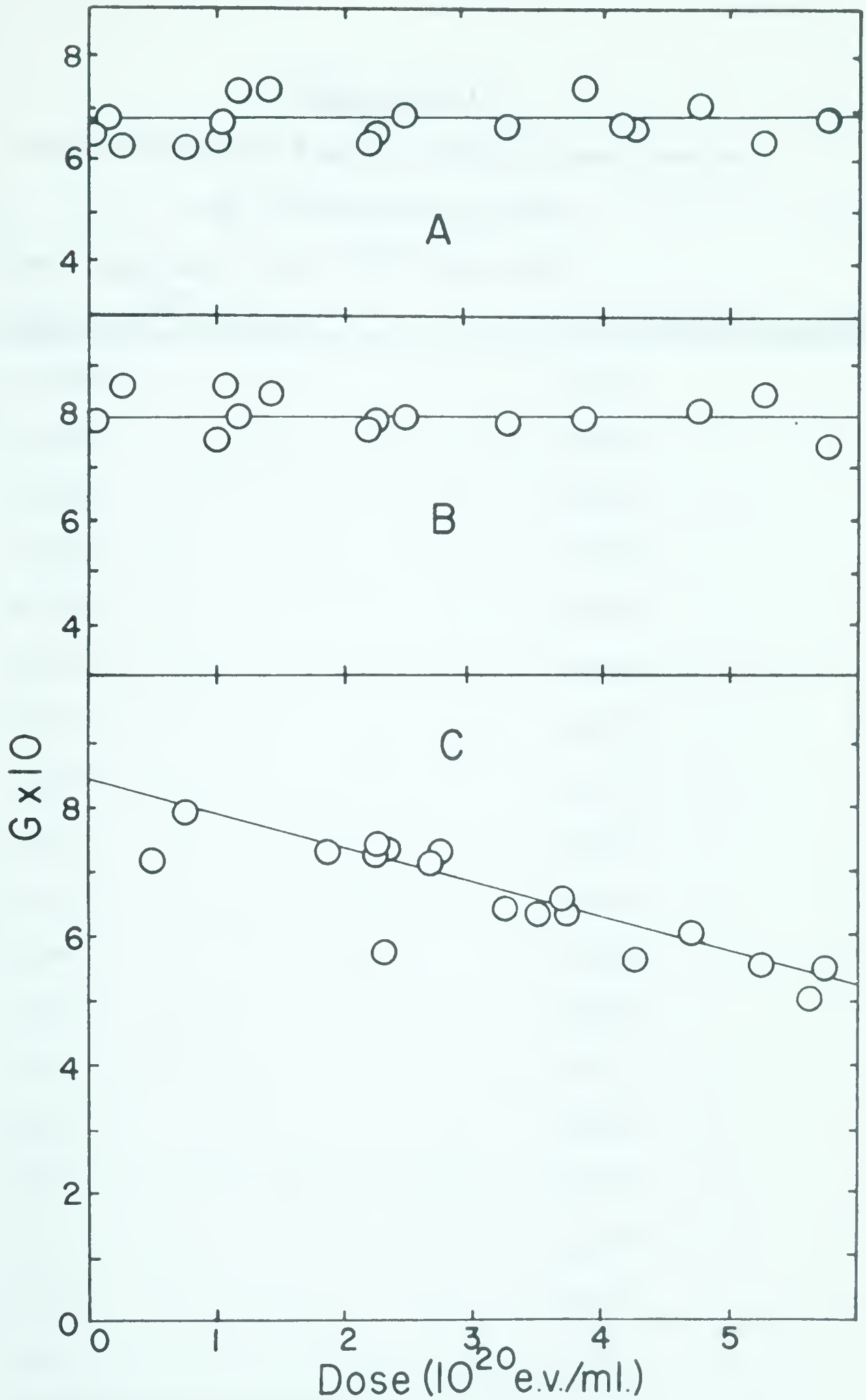

A
B
C
8
6
4
8
6
4
G x 10
8
6
4
2
0
0
1
2
3
4
5
Dose (10^20 e.v./ml.)

TABLE III 17

Carbon Monoxide Yields from Cyclopentanone, as a Function of Dose.

Dose rate range = 2 ÷ 11 (10^{18} eV/ml hr)

Dose (10^{20} eV/ml)	G (Carbon monoxide)
0.0505	0.65
0.150	0.68
0.250	0.62
0.754	0.62
0.982	0.63
1.04	0.67
1.15	0.73
1.39	0.73
2.17	0.63
2.25	0.65
2.46	0.69
3.25	0.66
3.85	0.73
4.12	0.66
4.25	0.65
4.75	0.70
5.25	0.63
5.75	0.67

TABLE III 18

Ethylene Yields from Cyclopentanone, as a Function of Dose.

Dose rate range = 2 - 11 (10^{18} eV/ml hr)

Dose (10^{20} eV/ml)	G (Ethylene)
0.0505	0.79
0.250	0.86
0.982	0.75
1.04	0.86
1.15	0.80
1.39	0.85
2.17	0.77
2.25	0.79
2.46	0.82
3.25	0.78
3.85	0.79
4.75	0.81
5.25	0.84
5.75	0.73

TABLE III 19

4-Pentenal Yields from Cyclopentanone,

as a Function of Dose.

Dose rate range = 2 - 11 (10^{18} eV/ml hr)

Dose (10^{20} eV/ml)	G (4-Pentenal)*
0.508	0.72
0.751	0.79
1.85	0.73
2.25	0.73
2.28	0.74
2.32	0.57
2.45	0.74
2.66	0.71
2.78	0.73
3.25	0.64
3.50	0.63
3.69	0.66
3.75	0.63
4.27	0.56
4.70	0.60
5.25	0.55
5.64	0.50
5.75	0.55

* Measurable on the Ucon column only, because of VPC conditions used.

TABLE III 20

The Initial Yields of the Major Products Arising from the C-C Bond Cleavage of Cyclopentanone.

Product	G_i*
Carbon monoxide	0.68 ± 0.06
Ethylene	0.80 ± 0.04
4-Pentenal	0.84 ± 0.10

* G values extrapolated to zero dose. The limits were estimated visually from the appropriate graphs.

FIGURE III 8

Yields of Minor Gaseous Products Arising from C-C Bond Cleavage from Liquid Cyclopentanone.

A: Ethane

B: Acetylene

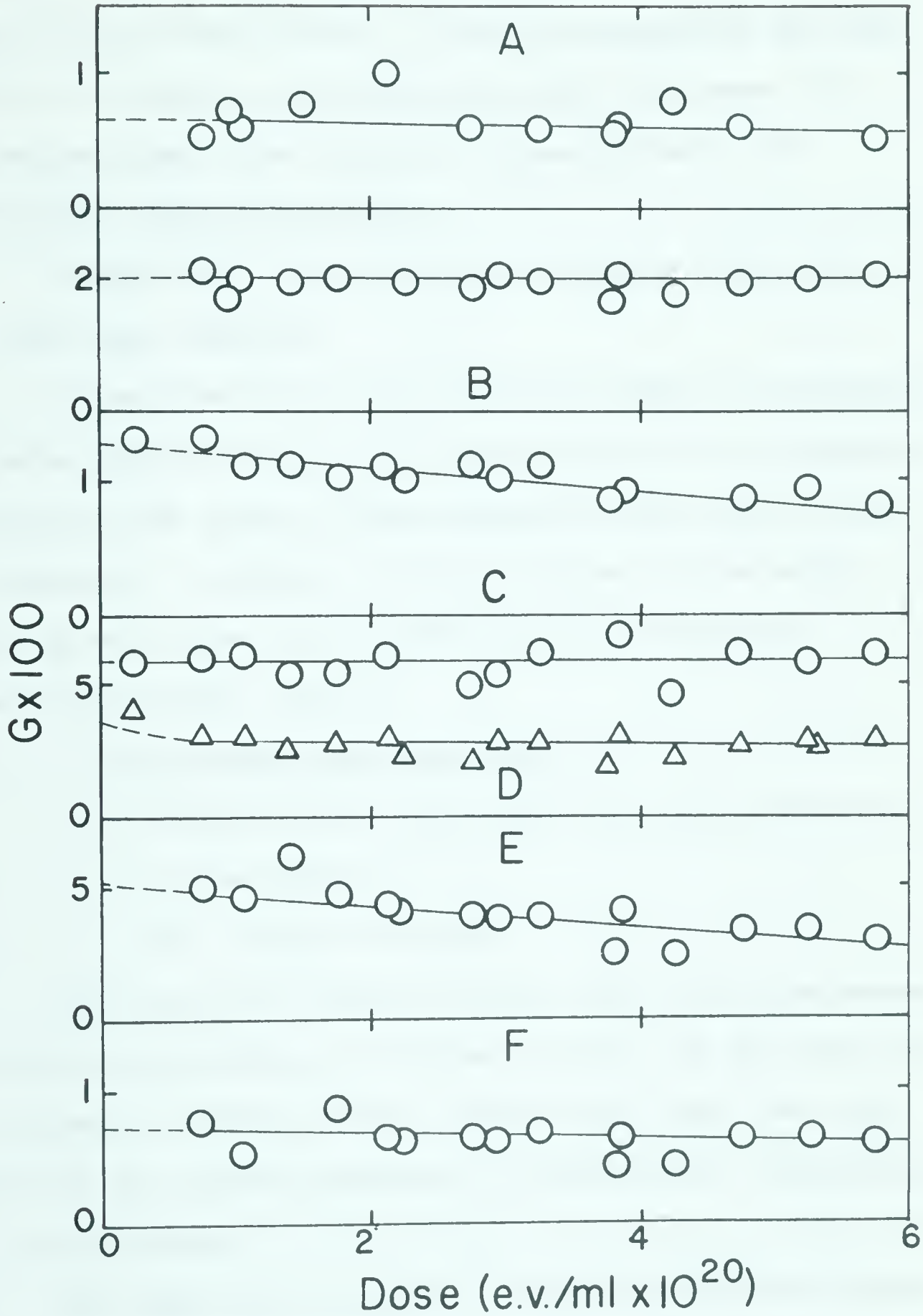
C: Propylene

D: ○ Cyclobutane

△ n-Butane

E: 1-Butene

F: Methylcyclopropane


A
B
C
D
E
F
1
0
2
0
1
0
5
0
5
0
1
0
Gx100
0
2
4
6
Dose (e.v./ml x 10^20)

The data used in this plot are listed in Tables III 21, III 22, III 23 and III 24. With the exception of the yields of propylene and 1-butene which decrease with increasing dose, the yields of these products are essentially dose-independent.

Methane was also found as a product from some of the high dose samples.

Determinations of the initial yields of the minor products shown in Fig. III 8 would not be very reliable because of the rather large extrapolations which would be required. A summary of the G values of the minor products at a dose of 1×10^{20} eV/ml is therefore presented in Table III 25.

2. Cyclopentanone Solutions

a. Cyclopentanone Solutions Containing Benzene or 1,3-Pentadiene

(1) Carbon monoxide

The yield of carbon monoxide from cyclopentanone/pentadiene solutions is plotted in Fig. III 9A from the data given in Table III 26. These data show that the formation of carbon monoxide is inhibited by the addition of 1,3-pentadiene.

The addition of benzene to cyclopentanone causes a slight sensitization of the formation of carbon monoxide. The yields of CO from these solutions are presented in Table III 27 and Fig. III 9B. The two dose rates used

TABLE III 21

Yields of Ethane and Acetylene from Cyclopentanone, as a Function of Dose.

Dose rate range = 2 - 11 (10^{18} eV/ml hr.)

Dose (10^{20} eV/ml)	G (Ethane)	G (Acetylene)
0.754	0.006	0.021
0.950	0.007	0.017
1.04	0.006	0.020
1.39	-	0.019
1.50	0.008	-
1.75	-	0.020
2.12	0.010	-
2.25	-	0.019
2.75	0.006	0.018
2.93	-	0.020
3.25	0.006	0.019
3.78	0.006	0.016
3.85	0.006	0.020
4.25	0.008	0.017
4.75	0.006	0.019
5.25	-	0.020
5.75	0.005	0.020

TABLE III 22

Yields of Propylene and Cyclobutane from Cyclopentanone, as a Function of Dose.

Dose rate range = 2 - 11 (10^{18} eV/ml hr)

Dose (10^{20} eV/ml)	G (Propylene)	G (Cyclobutane)
0.250	0.013	0.057
0.754	0.013	0.059
1.04	0.011	0.061
1.39	0.011	0.053
1.75	0.010	0.054
2.12	0.011	0.061
2.25	0.010	-
2.75	0.011	0.049
2.93	0.010	0.054
3.25	0.011	0.062
3.78	0.008	-
3.85	0.009	0.068
4.25	-	0.046
4.75	0.009	0.062
5.25	0.009	0.058
5.75	0.008	0.061

TABLE III 23

Yields of n-Butane and 1-Butene from Cyclopentanone, as a Function of Dose.

Dose rate range = 2 - 11 (10^{18} eV/ml hr)

Dose (10^{20} eV/ml)	G (n-Butane)	G (1-Butene)
0.250	0.041	-
0.754	0.030	0.049
1.04	0.030	0.045
1.39	0.024	0.062
1.75	0.028	0.046
2.12	0.030	0.042
2.25	0.023	0.040
2.75	0.021	0.039
2.93	0.028	0.037
3.25	0.028	0.038
3.78	0.019	0.025
3.85	0.030	0.040
4.25	0.022	0.024
4.75	0.027	0.033
5.25	0.029	0.034
5.34	0.026	-
5.75	0.029	0.030

TABLE III 24

Yields of Methylcyclopropane from Cyclopentanone, as a Function of Dose.

Dose rate range = 2 - 11 (10^{18} eV/ml hr)

Dose (10^{20} eV/ml)	G (Methylcyclopropane)
0.754	0.007
1.04	0.005
1.75	0.008
2.12	0.006
2.25	0.006
2.75	0.006
2.93	0.006
3.25	0.007
3.78	0.004
3.85	0.006
4.25	0.004
4.75	0.006
5.25	0.006
5.75	0.006

TABLE III 25

Yields of Minor Gaseous Products Arising from C-C Bond Cleavage.

Product	G*
Methane	<0.005
Ethane	~ 0.007
Acetylene	0.020 ± 0.004
Propylene	0.011 ± 0.003
n-Butane	0.028 ± 0.010
Methylcyclopropane	0.007 ± 0.002
1-Butene	0.047 ± 0.010
Cyclobutane	0.060 ± 0.010

* G values at a dose of 1×10^{20} eV/ml

FIGURE III 9

Yields of Carbon Monoxide from Solutions.

ϵ_s = electron fraction of solute

Dashed line refers to G_{ex}

Dose = 8.0 $\pm$ 0.1 (10^{-4} eV/e^-), about 2 x 10^{20} eV/ml.

A: 1,3-Pentadiene solutions, Dose rate = 17.3 x 10^{-5} eV/e^- hr.

B: Benzene solutions

● dose rate = 0.66 x 10^{-5} eV/e^- hr

○ dose rate = 17.3 x 10^{-5} eV/e^- hr

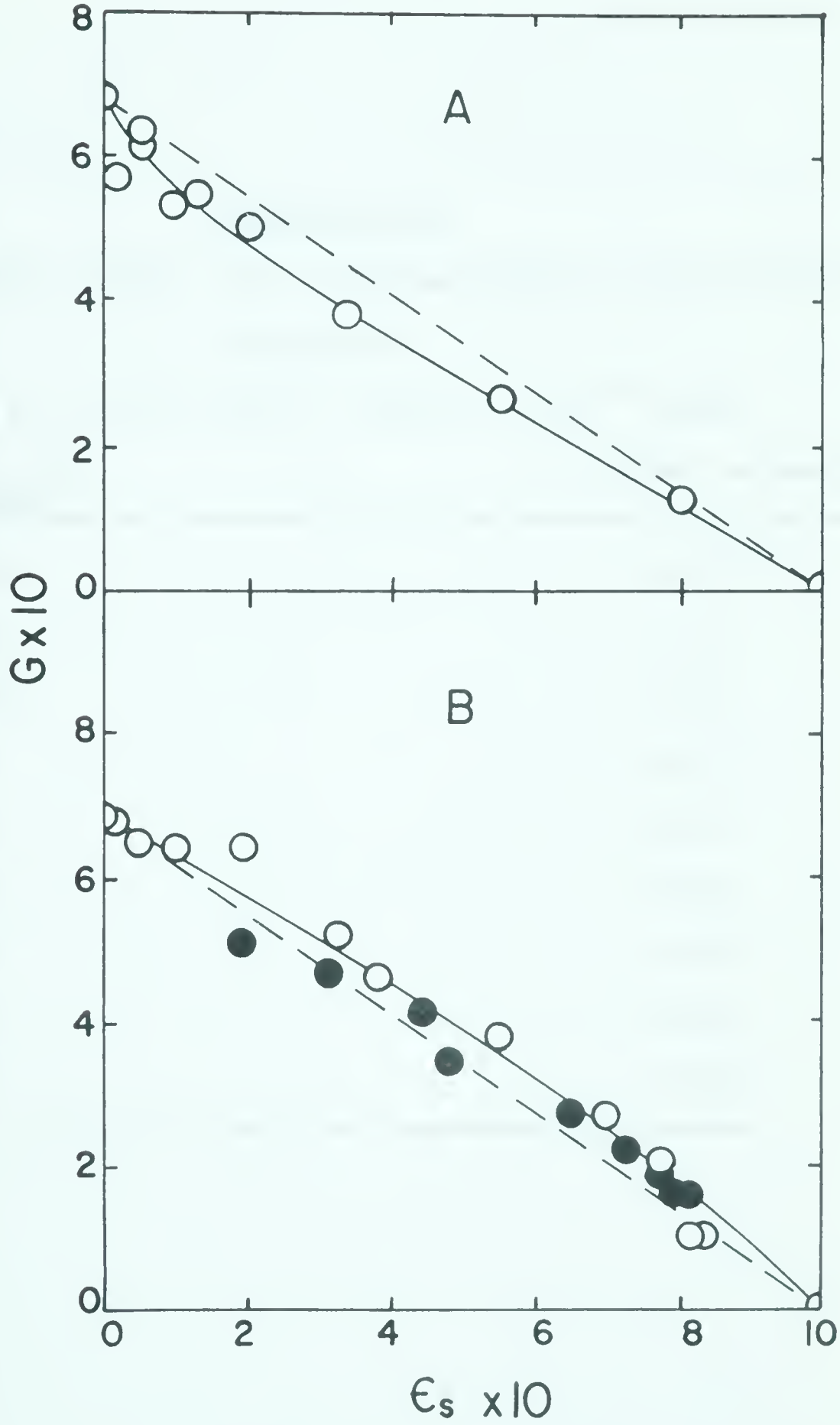

A
B
G x 10
ϵ_s x 10
0
2
4
6
8
10

TABLE III 26

Carbon Monoxide Yields from Cyclopentanone/1,3-Pentadiene Solutions.

Dose = 8.0 ± 0.1 (10^{-4} eV/e^-), about 2 x 10^{20} eV/ml

Electron Fraction 1,3-Pentadiene	G (Carbon monoxide)
0.0206	0.57
0.0516	0.61
0.0529	0.63
0.100	0.53
0.131	0.55
0.199	0.50
0.344	0.39
0.548	0.26
0.797	0.11

TABLE III 27

Carbon Monoxide Yields from Cyclopentanone/Benzene Solutions.

Dose = 8.0 ± 0.1 (10^{-4} eV/e$^-$), about 2 x 10^{20} eV/ml

Electron Fraction Benzene	G (Carbon monoxide) A	B
0.0208	0.68	-
0.0554	0.65	-
0.101	0.64	-
0.193	-	0.51
0.194	0.64	-
0.313	-	0.47
0.325	0.52	-
0.377	0.46	-
0.437	-	0.41
0.485	-	0.34
0.555	0.38	-
0.647	-	0.27
0.698	0.27	-
0.732	-	0.22
0.778	0.20	-
0.785	-	0.19
0.801	-	0.16
0.823	0.10	-
0.826	-	0.16
0.842	0.10	-

A: Dose rate = 17.3 ± 0.2 (10^{-5} eV/e$^-$ hr)

B: Dose rate = 0.66 ± 0.03 (10^{-5} eV/e$^-$ hr)

(17.3×10^{20} eV/e$^-$ hr and 0.66×10^{-5} eV/e$^-$ hr) are differentiated in both the table and the figure and no dose rate effect is indicated.

(2) Ethylene

The inhibition of the formation of ethylene by pentadiene is shown by the data presented in Table III 28 and Fig. III 10A. The G value for ethylene from 1,3-pentadiene is 0.020 at a dose rate of 17.3×10^{-5} eV/e$^-$ hr and a total dose of 8.0×10^{-4} eV/e$^-$.

Benzene causes a slight sensitization of the yield of this product as indicated by the data in Table III 29 and Fig. III 10B, and there is no dose rate effect.

(3) 4-Pentenal

The formation of pentenal is stronglyinhibited by the addition of 1,3-pentadiene as shown in Figs. III 11A and III 11B, which were constructed from the data presented in Table III 30. The G value of this product from samples containing an electron fraction of the diene of 0.01 is about 41% of that obtained from pure cyclopentanone at the same dose and is only about 35% of G_i (4-pentenal). The initial rapid decrease in the pentenal yield with increasing pentadiene concentration is followed by a slower rate of decrease as the diene concentration is increased above an electron fraction of 0.01 (Fig. III 11).

The yield of 4-pentenal is stronglysensitized by

FIGURE III 10

Yields of Ethylene from Solutions.

ϵ_s = electron fraction of solute

Dashed line refers to G_{ex}

Dose = 8.0 ± 0.1 (10^{-4} eV/e^-), about 2 x 10^{20} eV/ml.

A: 1,3-Pentadiene solutions, Dose rate = 17.3 x 10^{-5} eV/e^- hr.

B: Benzene solutions

● Dose rate = 0.66 x 10^{-5} eV/e^- hr.

○ Dose rate = 17.3 x 10^{-5} eV/e^- hr.

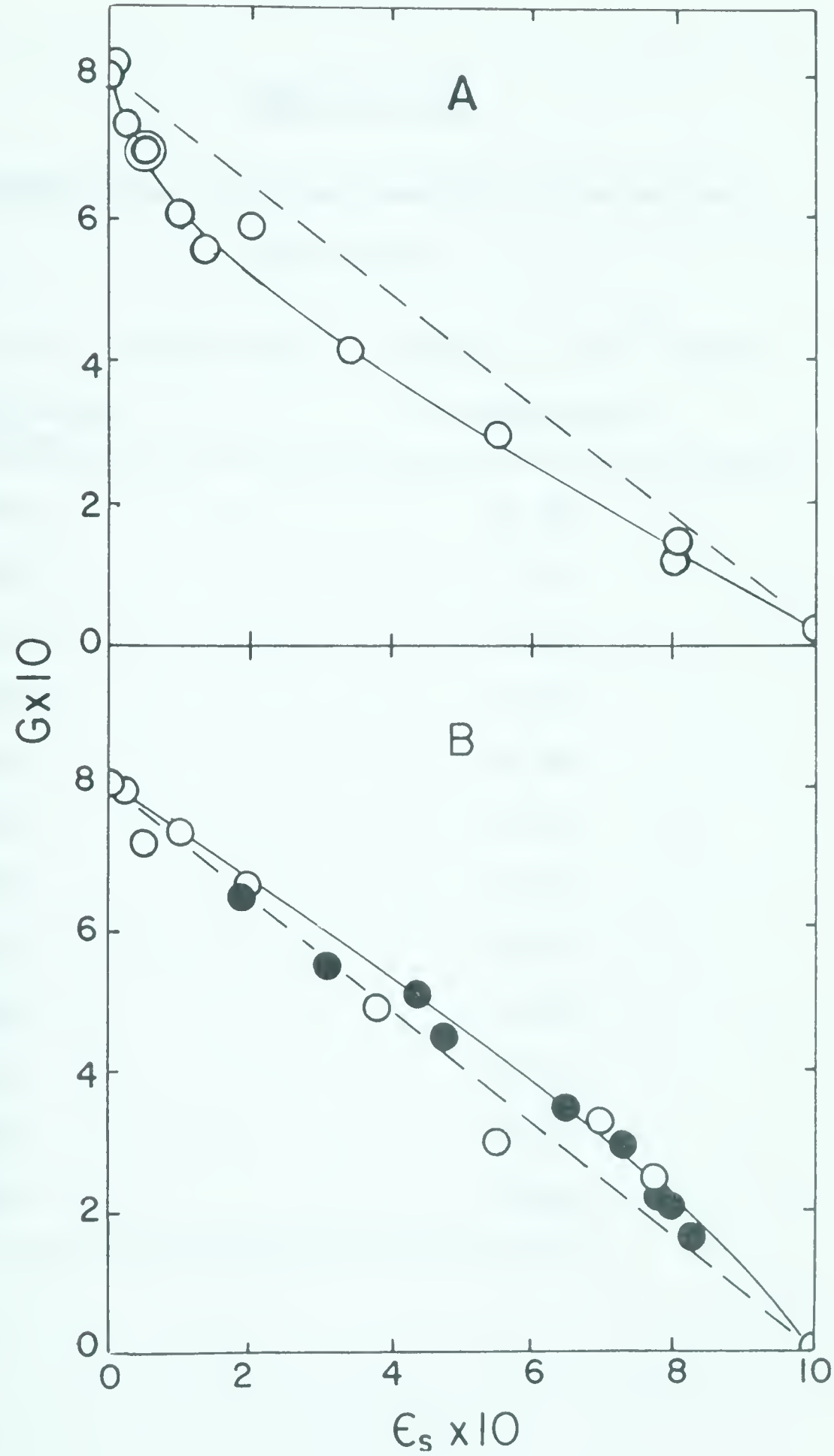

A
B
8
6
4
2
0
0
2
4
6
8
10
G x 10
ϵ_s x 10

TABLE III 28

Ethylene Yields from Cyclopentanone/1,3-Pentadiene Solutions.

Dose = 8.0 ± 0.1 (10^{-4} eV/e^-), about 2 x 10^{20} eV/ml

Electron Fraction 1,3-Pentadiene	G (Ethylene)
0.0043	0.82
0.0206	0.73
0.0516	0.69
0.0529	0.69
0.100	0.60
0.131	0.55
0.199	0.59
0.344	0.41
0.548	0.29
0.795	0.13
0.797	0.12
1.000	0.020

TABLE III 29

Ethylene Yields from Cyclopentanone/Benzene Solutions.

Dose = 8.0 ± 0.1 (10^{-4} eV/e^-), about 2 x 10^{20} eV/ml

Electron Fraction Benzene	G (Ethylene) A	B
0.0208	0.79	-
0.0554	0.72	-
0.101	0.73	-
0.193	-	0.64
0.194	0.65	-
0.313	-	0.54
0.377	0.48	-
0.437	-	0.50
0.485	-	0.44
0.555	0.29	-
0.647	-	0.34
0.698	0.32	-
0.732	-	0.28
0.784	0.24	-
0.785	-	0.21
0.801	-	0.20
0.826	-	0.16
1.000	~0	~0

A: Dose rate = 17.3 ± (10^{-5} eV/e^- hr)

B: Dose rate = 0.66 ± (10^{-5} eV/e^- hr)

FIGURE III 11

Yields of 4-Pentenal from Solution.

ϵ_s = electron fraction of solute

Dashed line refers to G_{ex}

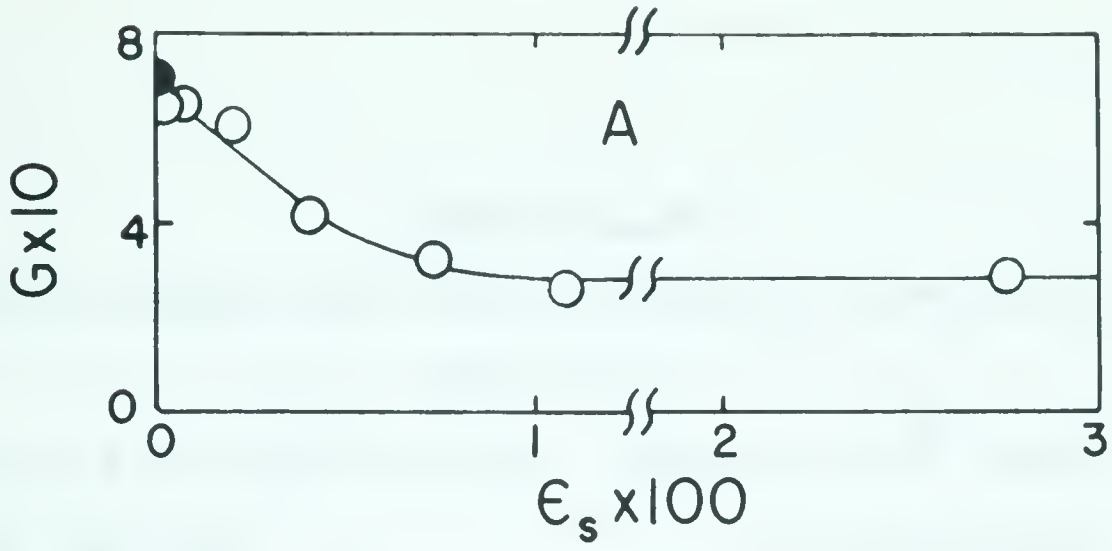
Dose = 8.0 ± 0.1 (10^{-4} eV/e^-), about 2 x 10^{20} eV/ml

A: 1,3-Pentadiene solutions

B: ○ 1,3-Pentadiene solutions

◒ Benzene solutions

● Pure cyclopentanone


A
8
4
0
0
1
2
3
G x 10
ϵ_s x 100

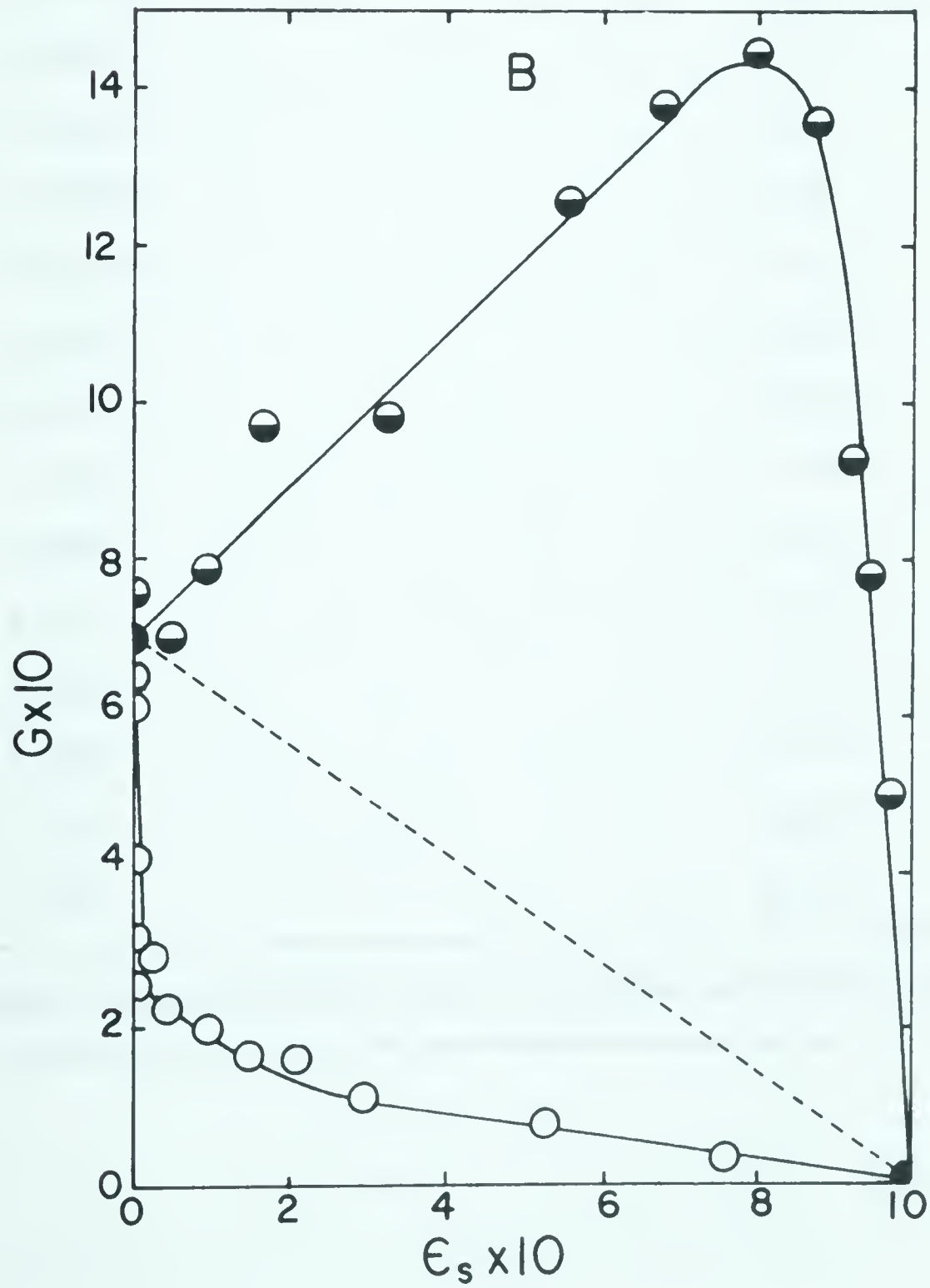

B
14
12
10
8
6
4
2
0
0
2
4
6
8
10
G x 10
ϵ_s x 10

TABLE III 30

4-Pentenal Yields from Cyclopentanone/1,3-Pentadiene Solutions.

Dose = 8.0 ± 0.1 (10^{-4} eV/e$^-$), about 2 x 10^{20} eV/ml

Electron Fraction 1,3-Pentadiene	G (4-Pentenal)*
0.00027	0.65
0.00107	0.65
0.00215	0.61
0.00425	0.42
0.00758	0.32
0.0111	0.26
0.0277	0.29
0.0520	0.23
0.0987	0.20
0.151	0.17
0.212	0.16
0.299	0.11
0.530	0.08
0.765	0.04

* Average value obtained from Carbowax and Ucon columns.

benzene as shown by Fig. III 11B and Table III 31. The maximum yield of the aldehyde (G $\sim$1.5) is obtained at an electron fraction of benzene of about 0.8. G (4-pentenal) at this benzene concentration is about twice that obtained from pure cyclopentanone. All the G values reported in this work were calculated on the basis of the total amount of energy absorbed by the solutions.

Two samples which contained equal electron fractions of benzene and cyclopentanone together with an electron fraction of 1,3-pentadiene of 0.01 gave yields of 4-pentenal of 0.31 G units. Binary solutions of the ketone with 0.01 electron fraction of the diene or 0.50 of benzene would give aldehyde yields of 0.28 or 1.18, respectively. The diene thus inhibits the sensitization effect of benzene.

(4) Minor gaseous products (G $<$0.1) from cyclopentanone/ benzene solutions.

The effects of added benzene on the yields of acetylene, propylene, n-butane, 1-butene, cyclobutane and methylcyclopropane are illustrated in Fig. III 12. The data are also presented in Tables III 32, III 33, and III 34. The yield of n-butane appears to be unaffected by the addition of benzene. The formation of each of the other products appears to be slightly sensitized by benzene.

(5) Minor gaseous products (G $<$0.1) from cyclopentanone/1,3-pentadiene solutions.

Analytical problems prevented measurement of the

TABLE III 31

4-Pentenal Yields from Cyclopentanone/Benzene Solutions.

Dose = 8.0 ± 0.1 (10^{-4} eV/e^-), about 2 x 10^{20} eV/ml

Electron Fraction Benzene	G (4-Pentenal)*
0.0203	0.76
0.0554	0.70
0.0945	0.79
0.177	0.97
0.343	0.98
0.561	1.26
0.682	1.38
0.799	1.45
0.875	1.36
0.925	0.93
0.951	0.78
0.977	0.50

* Average value obtained from Carbowax and Ucon columns.

FIGURE III 12

Yields of Minor Gaseous Products ($G < 0.1$) from Cyclopentanone/Benzene Solutions.

ϵ_s = electron fraction of solute

Dose = 8.0 ± 0.1 (10^{-4} eV/e^-), about 2×10^{20} eV/ml

Dose rate = 0.66×10^{-5} eV/e^- hr

A: Cyclobutane

B: Methylcyclopropane

C: 1-Butene

D: n-Butane

E: Propylene

F: Acetylene

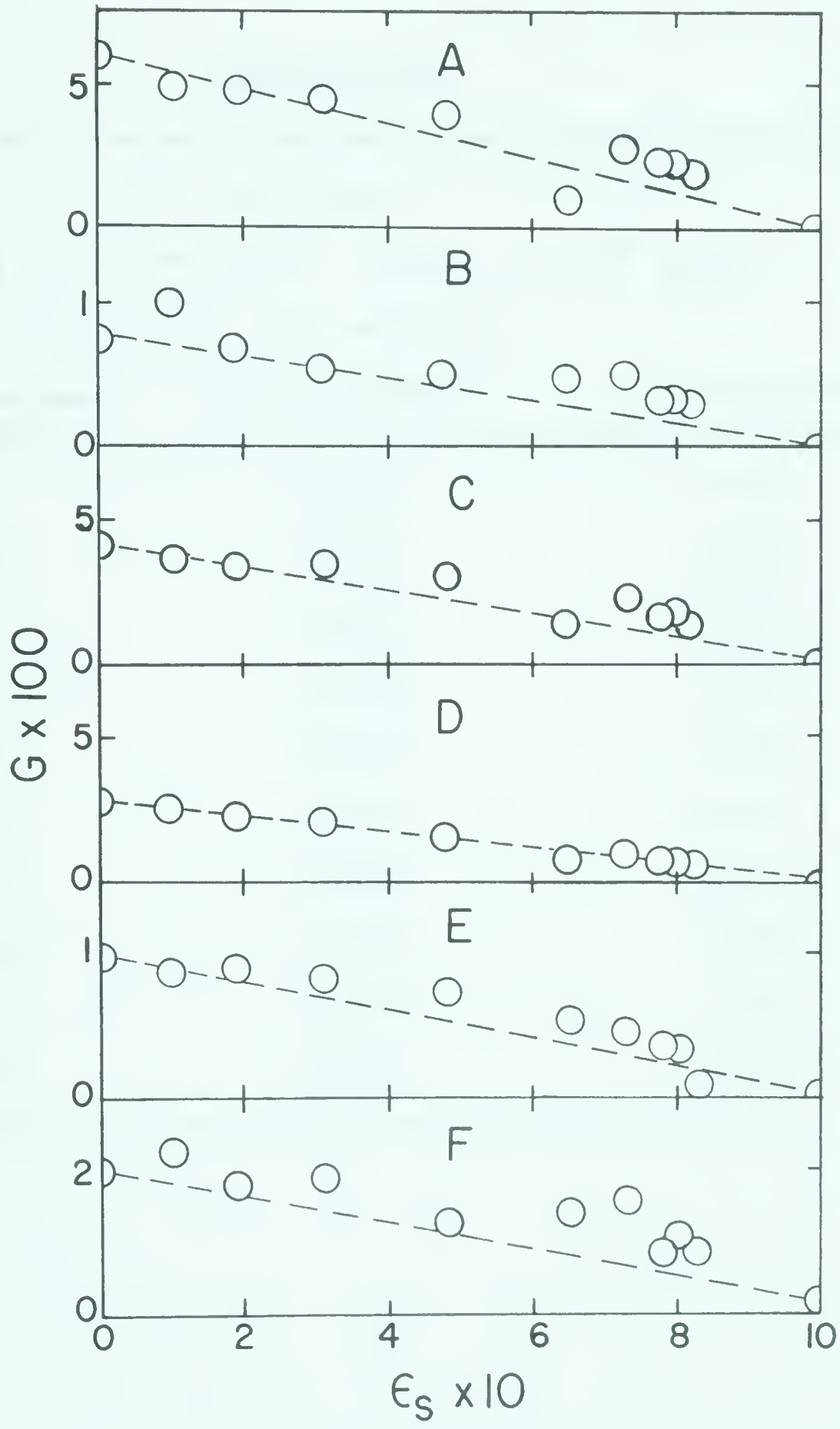

A
B
C
D
E
F
5
0
1
0
5
0
5
0
1
0
2
0
0
2
4
6
8
10
G x 100
ϵ_s x 10

TABLE III 32

Yields of Propylene and Acetylene from Cyclopentanone/ Benzene Solutions.

Dose = 8.0 ± 0.1 (10^{-4} eV/e$^-$), about 2 x 10^{20} eV/ml

Dose rate = 0.66 ± 0.03 (10^{-5} eV/e$^-$ hr)

Electron Fraction Benzene	G (Propylene)	G (Acetylene)
0	0.008	0.021
0.100	0.009	0.023
0.193	0.009	0.018
0.313	0.008	0.019
0.485	0.007	0.013
0.647	0.005	0.014
0.732	0.005	0.016
0.785	0.004	0.009
0.801	0.004	0.011
0.826	0.001	0.009

TABLE III 33

Yields of n-Butane and 1-Butene from Cyclopentanone/Benzene Solutions.

Dose = 8.0 ± 0.1 (10^{-4} eV/e^-), about 2 x 10^{20} eV/ml

Dose rate = 0.66 ± 0.03 (10^{-5} eV/e^- hr)

Electron Fraction Benzene	G (n-Butane)	G (1-Butene)
0	0.031	0.041
0.100	0.027	0.035
0.193	0.024	0.033
0.313	0.022	0.034
0.485	0.017	0.029
0.647	0.009	0.013
0.732	0.011	0.021
0.785	0.008	0.016
0.801	0.008	0.017
0.826	0.007	0.013

TABLE III 34

Yields of Methylcyclopropane and Cyclobutane from Cyclopentanone/Benzene Solutions.

Dose = 8.0 ± 0.1 (10^{-4} eV/e$^-$), about 2 x 10^{20} eV/ml

Dose rate = 0.66 ± 0.03 (10^{-5} eV/e$^-$ hr)

Electron Fraction Benzene	G (Methylcyclopropane)	G (Cyclobutane)
0	0.008	0.061
0.100	0.010	0.048
0.193	0.006	0.047
0.313	0.005	0.044
0.485	0.005	0.038
0.647	0.004	0.008
0.732	0.005	0.027
0.785	0.003	0.023
0.801	0.003	0.022
0.826	0.003	0.018

yields of these products as a function of the pentadiene concentration.

b. Cyclopentanone/Oxygen Samples

(1) Liquid phase at room temperature

Several 2 ml liquid phase samples of the ketone containing varying amounts of oxygen were irradiated to determine the effect of this additive on the yield of 4-pentenal. The concentrations of dissolved oxygen in these samples (electron fractions of 3.9 - 24 x 10^{-5}) were calculated assuming a solubility of 0.2 ml of oxygen per ml of ketone. This value is that given for some oxygenated compounds in the International Critical Tables (Loomis, 1928). Doses of about 3 x 10^{-4} eV/e^- were used for these samples. A rapid reduction of the yield of 4-pentenal by added oxygen is shown in Fig. III 13A and in Table III 35. An electron fraction of oxygen of 2 x 10^{-4} reduces the aldehyde yield to about 40% of that obtained from pure cyclopentanone at the same dose, or about 33% of G_i (4-pentenal). This same decrease in the 4-pentenal yield required about 100 times greater concentration of pentadiene than it did of oxygen (about 50 times greater, based on molarities).

The yields of other major products measured from these samples are also shown in Fig. III 13, and a summary of the data appears in Table III 35 and III 36. The yield of ethylene is very slightly decreased by oxygen, as

FIGURE III 13

Yields of Major Products ($G > 0.1$) from Cyclopentanone/Oxygen Solutions.

Dose = 3.1 ± 0.2 (10^{-4} eV/e^-)

A: 4-Pentenal

B: Ethylene

C: Cyclopentanol

D: Cyclopentenone

E: Carbon dioxide

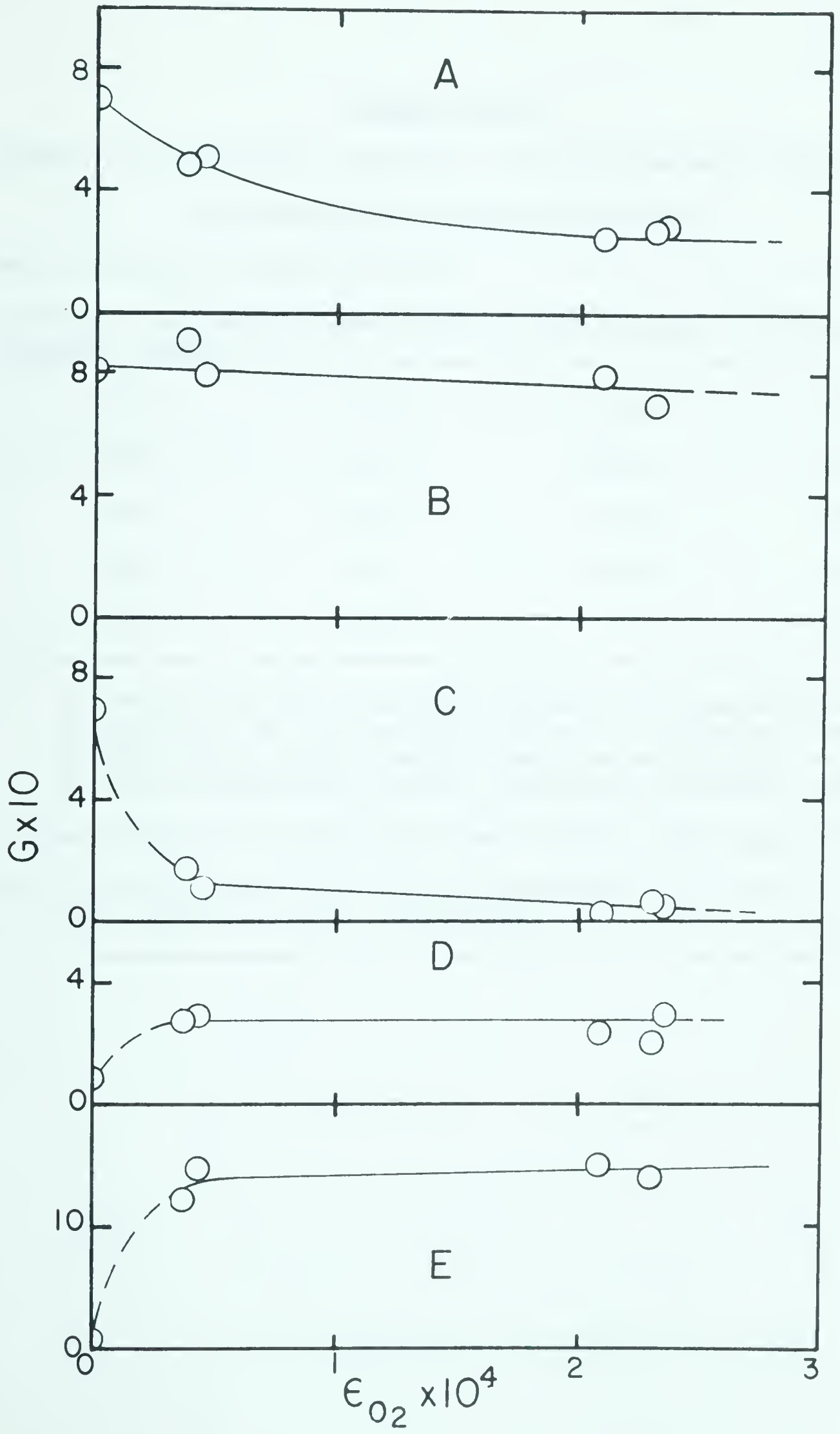

A
B
C
D
E
8
4
0
8
4
0
8
4
0
4
0
10
0
0
1
2
3
G x 10
$\epsilon_{O_2} \times 10^4$

TABLE III 35

Yields of 4-Pentenal, Ethylene and Cyclopentanol from Cyclopentanone/Oxygen Solutions.

Dose = 3.1 ± 0.2 (10^{-4} eV/e$^-$)

Electron Fraction Oxygen ($x10^4$) *	G(4-Pentenal) **	G(Ethylene)	G(Cyclopentanol) ***
0.39	0.48	0.90	0.17
0.45	0.50	0.80	0.11
2.10	0.24	0.81	0.03
2.31	0.27	0.70	0.06
2.37	0.28	-	0.05

* To calculate the electron fraction of dissolved oxygen, its solubility was assumed to be 0.2 ml/ml of the ketone on the basis of the values for the solubility of oxygen in some oxygenated organic compounds (Loomis, 1928).

** Average value obtained from Carbowax and Ucon columns.

*** The detection limit of cyclopentanol was about 0.05 for these analysis conditions.

TABLE III 36

Yields of Cyclopentenone and Carbon Dioxide from Cyclopentanone/Oxygen Solutions.

Dose = 3.1 ± 0.2 (10^{-4} eV/e$^-$)

Electron Fraction Oxygen ($x10^4$) *	G (Cyclopentenone)	G (Carbon dioxide)
0.39	0.27	1.23
0.45	0.29	1.45
2.10	0.23	1.52
2.31	0.19	1.41
2.37	0.29	-

* To calculate the electron fraction of dissolved oxygen, its solubility was assumed to be 0.2 ml/ml of the ketone on the basis of the values for the solubility of oxygen in some oxygenated organic compounds (Loomis, 1928).

illustrated in Fig. III 13B. The G value of cyclopentanol is reduced to below its limit of detection ($G < 0.05$ under these analytical conditions) by an electron fraction of oxygen of about 3×10^{-4} (see Fig. III 13C). The addition of oxygen causes an increased yield of cyclopentenone as shown in Fig. III 13D. Carbon dioxide was detected as a new product from these oxygen-containing samples and its yield increases slightly with increasing oxygen concentration as illustrated in Fig. III 13E.

The effects of dissolved oxygen on the yields of the minor ($G < 0.1$) gaseous products which arise from the radiolysis of liquid cyclopentanone are shown in Fig. III 14. The data used in constructing this figure are presented in Tables III 37 and 38. The yields of cyclobutane, methylcyclopropane, and acetylene are essentially unaffected by added oxygen (Figs. III 14A, B, and F respectively). The yield of 1-butene is reduced to about 40% of that obtained from pure cyclopentanone whereas n-butane and propylene are rapidly eliminated as products when oxygen is added (see Figs. III 14C, D, and E).

(2) Vapor phase at 130°C.

Several vapor phase samples were irradiated at $130^{\circ} \pm 5^{\circ}$C to determine if a similar reduction of the aldehyde yield by oxygen would be found. The high temperature was used to obtain a sufficiently high vapor

FIGURE III 14

Effects of Dissolved Oxygen on the Yields of Minor Products ($G < 0.1$) from the Liquid Phase Radiolysis of Cyclopentanone.

A: Cyclobutane

B: Methylcyclopropane

C: 1-Butene

D: n-Butane

E: Propylene

F: Acetylene

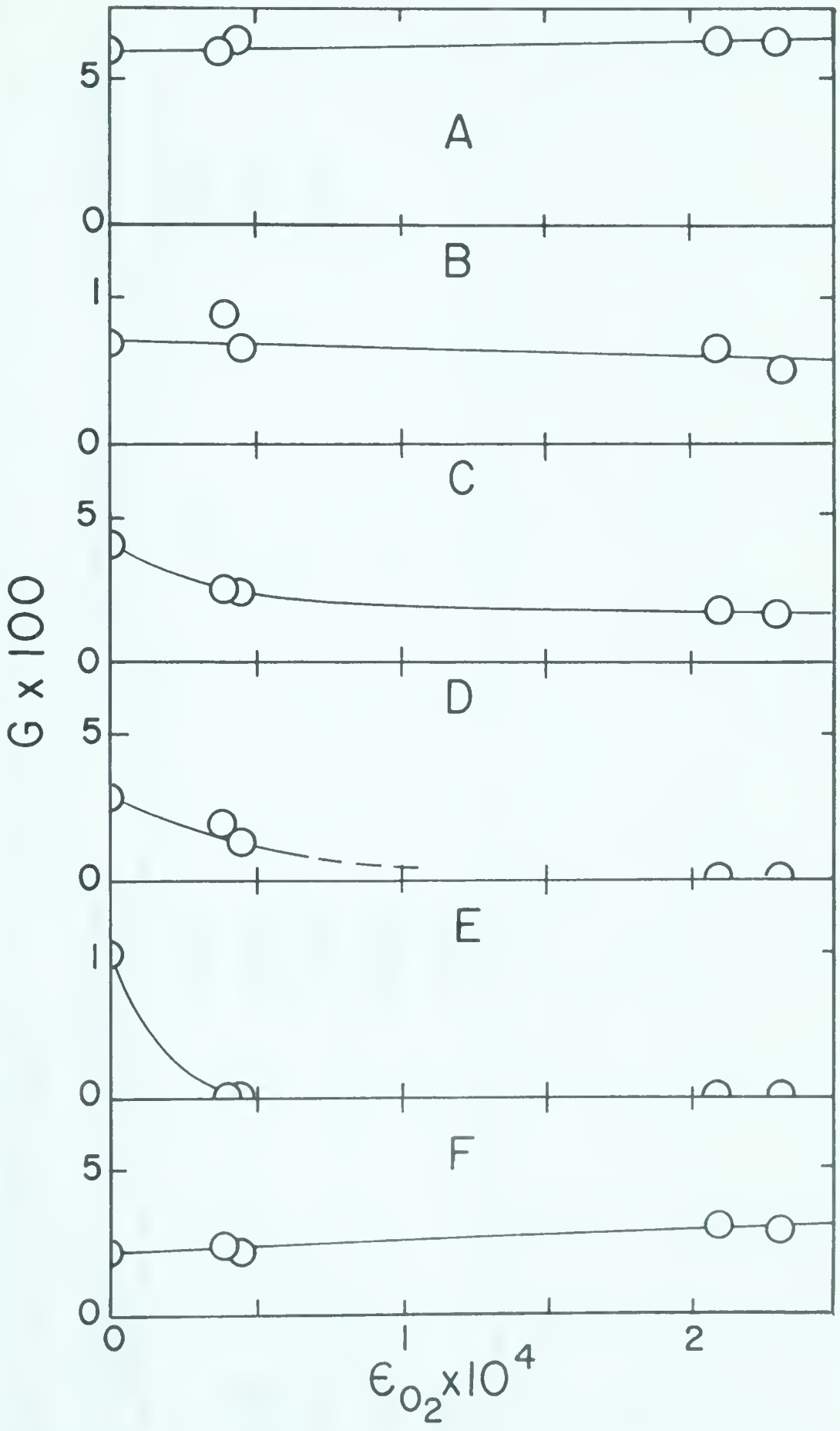

G x 100
5
0
A
B
1
0
C
5
0
D
5
0
E
1
0
F
5
0
0
1
2
$\epsilon_{O_2} \times 10^4$

TABLE III 37

Yields of Acetylene, Propylene and n-Butane from Cyclopentanone/Oxygen Solutions.

Dose = 3.1 $\pm$ 0.2 (10^{-4} eV/e^{-})

Electron Fraction Oxygen ($x10^4$)	G (Acetylene)	G (Propylene)	G (n-Butane)
0	0.020	0.010	0.028
0.39	0.024	0	0.018
0.45	0.021	0	0.012
2.10	0.030	0	0
2.31	0.029	0	0

TABLE III 38

Yields of 1-Butene, Methylcyclopropane, and Cyclobutane from Cyclopentanone/ Oxygen Solutions.

Dose = 3.1 $\pm$ 0.2 (10^{-4} eV/e$^-$)

Electron Fraction Oxygen (x 10^4)	G (1-Butene)	G (Methylcyclopropane)	G (Cyclobutane)
0	0.040	0.007	0.058
0.39	0.025	0.009	0.058
0.45	0.023	0.006	0.064
2.10	0.017	0.006	0.063
2.31	0.015	0.005	0.062

pressure of the ketone. The aldehyde yield decreased only slightly with increasing oxygen content (Fig. III 15A). Two facts should be noted, however: (1) the yield of 4-pentenal (G = 0.20) is only 29% of that found in the liquid phase radiolysis at 25°C; and (2) the yield of the aldehyde is not as stronglyaffected by oxygen in the vapor phase as it was in the liquid phase (compare with Fig. III 13A).

Other major products measured from these samples are also shown in Fig. III 15 and the yields are summarized in Tables III 39 and III 40. Ethylene (see Fig. III 15B) has a yield which is almost four times that found from room temperature liquid phase radiolyses, and which is essentially unaffected by the addition of oxygen. The yield of cyclopentanol is reduced to below the detection limit (about 0.05 G units under the analytical conditions used for these samples) by an electron fraction of oxygen of 4.5×10^{-3} (see Fig. III 15C). Cyclopentenone exhibited a steadily increasing yield with the addition of oxygen as shown in Fig. III 15D. The yield of CO_2 (see Fig. III 15E) also increases with increasing oxygen concentration and reaches a yield of about 18 G units at an electron fraction of oxygen of 0.03. Water, which was not measurable as a product from the liquid phase ketone/oxygen samples, was produced in considerable quantities in these vapor phase samples as shown in Fig. III

FIGURE III 15

Yields of Major Products from Cyclopentanone/Oxygen Vapor Phase Samples.

Dose = 7.6 ± 0.3 (10^{-4} eV/e$^-$)

A: 4-Pentenal

B: Ethylene

C: Cyclopentanol

D: Cyclopentenone

E: Carbon dioxide

F: Water

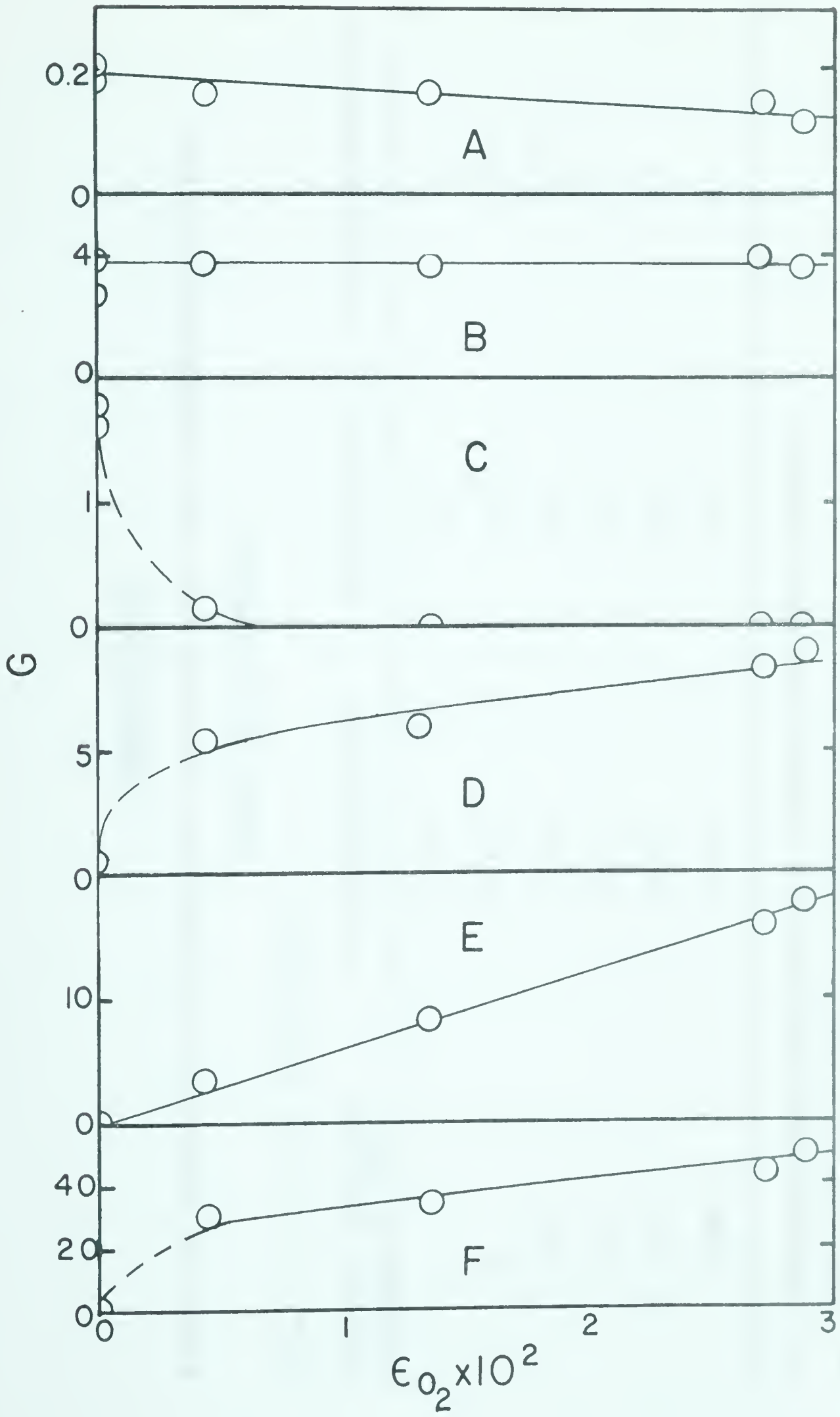

0.2
0
A
4
0
B
0
C
1
0
D
5
0
E
10
0
F
40
20
0
0
1
2
3
G
$\epsilon_{O_2} \times 10^2$

TABLE III 39

Yields of 4-Pentenal, Ethylene, and Cyclopentanol from Cyclopentanone/Oxygen Vapor Phase Samples.

Dose = 7.6 $\pm$ 0.3 (10^{-4} eV/e^-)

Electron Fraction Oxygen (x 10^2)	G (4-Pentenal)*	G (Ethylene)	G (Cyclopentanol)**
0	0.20	3.6	1.6
0	0.19	2.9	1.8
0.45	0.16	3.6	0.14
1.36	0.17	3.6	0
2.72	0.15	3.9	0
2.88	0.12	3.5	0

* Average value obtained from Carbowax and Ucon columns.

** The detection limit of cyclopentanol was 0.05 G units.

TABLE III 40

Yields of Cyclopentenone, Carbon Dioxide and Water from Cyclopentanone/Oxygen Vapor Phase Samples.

Dose = 7.6 ± 0.3 (10^{-4} eV/e^-)

Electron Fraction Oxygen (x 10^2)	G (Cyclopentenone)	G (Carbon dioxide)	G (Water)*
0	0.50	-	-
0	0.46	-	-
0.45	5.4	3.4	31.
1.36	5.6	8.2	35.
2.72	8.4	15.9	44.
2.88	8.8	17.9	51.

* These values have limits of $\pm$ 15%, and represent the average value obtained from Carbowax and Ucon columns.

15F. Analytical difficulties, caused partly by peak tailing, caused limits of ± 15% to be associated with these values which represent the average of the values obtained from the Ucon and Carbowax columns. A definite increase in G (water) with increasing oxygen concentration is indicated, however.

The effects of added oxygen on the yields of acetylene, propylene, n-butane, methylcyclopropane, 1-butene, and cyclobutane are shown in Fig. III 16, and the data are summarized in Tables III 41 and III 42. A comparison of the radiolytic yields of several products from the vapor phase (at 130°C) with yields obtained from the liquid phase samples (at 25°C) is presented in Table III 43. The only product which exhibited the same yield in both phases was cyclobutane. The yields of the other compounds listed were 2-13 times higher in the vapor phase. The yields of cyclobutane and acetylene are independent of the oxygen concentration (Figs. III 16A and F). n-Butane and propylene are eliminated as products by an electron fraction of oxygen at 0.0045 (see Figs. III 16D and E). The yields of methylcyclopropane and 1-butene decrease with increasing oxygen concentration but the olefin yield shows a more marked reduction (Figs. 16B and C). The effect of added oxygen on the yield of 1,3-butadiene is shown in Fig. III 16G. This product was not observed from the liquid phase radiolysis of

FIGURE III 16

Yields of Acetylene, Propylene and the C_4 Products from Cyclopentanone/Oxygen Vapor Phase Samples.

A: Cyclobutane

B: Methylcyclopropane

C: 1-Butene

D: n-Butane

E: Propylene

F: Acetylene

G: 1,3-Butadiene

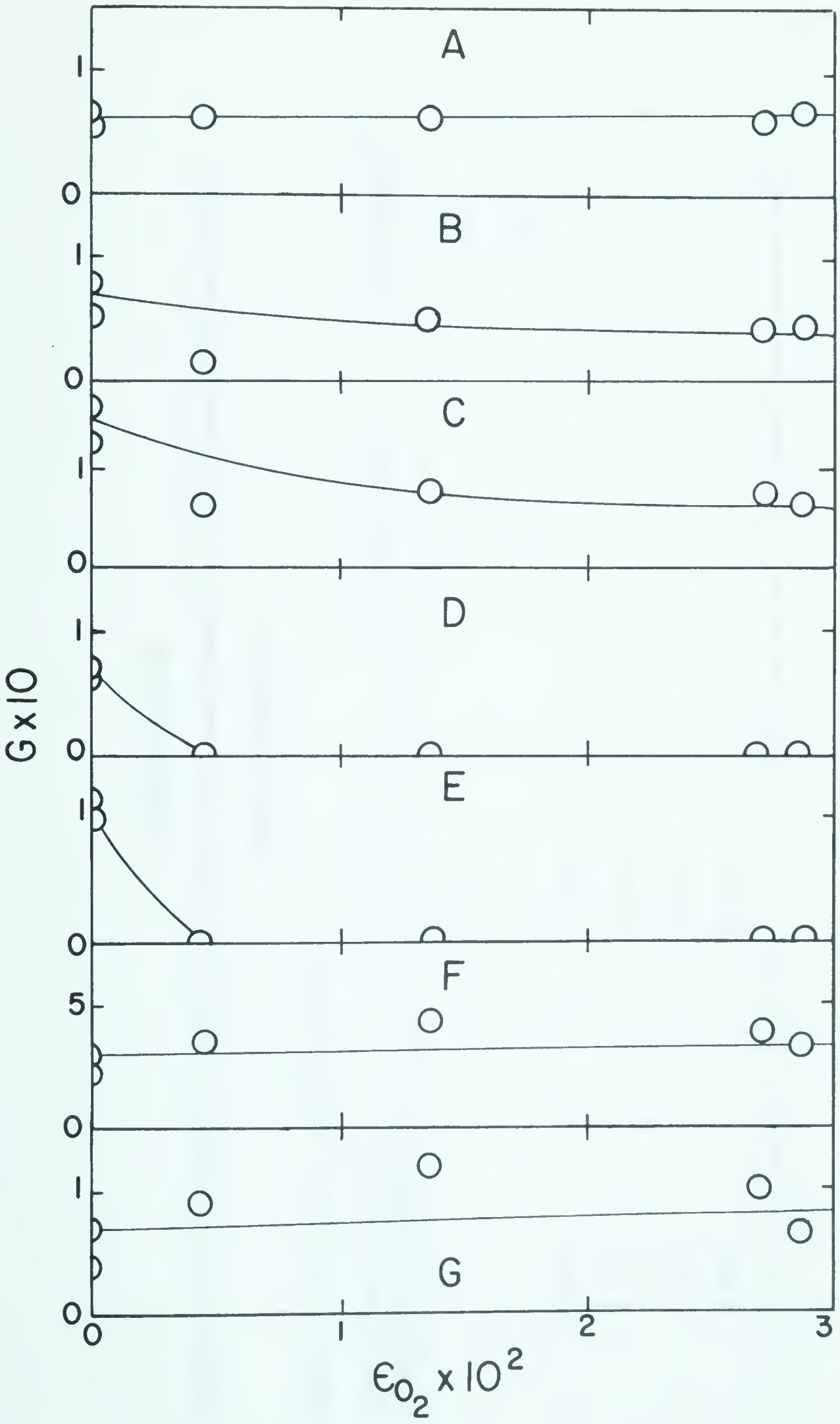

A
B
C
D
E
F
G
1
0
5
G x 10
0
1
2
3
$\epsilon_{O_2} \times 10^2$

TABLE III 41

Yields of Acetylene, Propylene and n-Butane from Cyclopentanone/Oxygen Vapor Phase Samples.

Dose = 7.6 $\pm$ 0.3 (10^{-4} eV/e^-)

Electron Fraction Oxygen (x 10^2)	G (Acetylene)	G (Propylene)	G (n-Butane)
0	0.27	0.11	0.068
0	0.22	0.10	0.060
0.45	0.36	0	0
1.36	0.42	0	0
2.72	0.38	0	0
2.88	0.31	0	0

TABLE III 42

Yields of 1-Butene, Methylcyclopropane, Cyclobutane, and 1,3-Butadiene from Cyclopentanone/Oxygen Vapor Phase Samples.

Dose = 7.6 ± 0.3 (10^{-4} eV/e$^-$)

Electron Fraction Oxygen (x 10^2)	G (1-Butene)	G (Methylcyclopropane)	G (Cyclobutane)	G (1,3-Butadiene)
0	0.130	0.055	0.058	0.040
0	0.160	0.078	0.067	0.069
0.45	0.063	0.015	0.060	0.087
1.36	0.072	0.049	0.063	0.120
2.72	0.074	0.041	0.057	0.100
2.88	0.063	0.045	0.065	0.061

TABLE III 43

Comparison of the Yields of Products Arising from C-C Bond Cleavage in the Liquid and Vapor Phases.*

Product	G Liquid Phase	G Vapor Phase	G vapor phase / G liquid phase
Ethylene	0.80	3.3	4
4-Pentenal	0.74	0.20	0.3**
Carbon monoxide	0.68	-	-
1-Butene	0.047	0.15	3
Cyclobutane	0.060	0.063	1
n-Butane	0.028	0.064	2
Methylcyclopropane	0.007	0.067	10
Acetylene	0.020	0.25	13
Propylene	0.010	0.11	11
1,3-Butadiene	-	0.055	-

* Vapor phase samples were irradiated at 130 ± 5°C while the liquid samples were irradiated at 25 ± 2°C.

** This ratio is not too meaningful because of the thermal decomposition of 4-Pentenal at this temperature. (See p.163).

cyclopentanone. It appears that the diene yield is either unaffected by oxygen or is slightly increased.

(3) Heated liquid phase

In order to determine whether the lower yield of 4-pentenal from the vapor phase samples irradiated at 130°C (as compared to the liquid phase samples at 25°C) was due to the change of state or to the change of temperature, several liquid samples were radiolyzed at 120° ± 5°C). The yield of 4-pentenal from the heated samples of pure cyclopentanone was about 0.23 G units, which is close to that obtained from the vapor phase at 130° C (G = 0.20). Oxygen did not affect the G value at concentrations up to 1×10^{-4} electron fraction. The lower dose rate available for the heated liquid ketone samples (4.9×10^{18} eV/g hr) required that they be heated for about ten times longer than the vapor phase samples (dose rate = 5.5×10^{19} eV/g hr) which were maintained at 130° for about six hours. Since the aldehyde yield was decreased by increasing the temperature, an attempt was made to determine whether this decrease was due to an adverse effect on the precursor(s) of 4-pentenal, or to the destruction of the aldehyde itself. Samples of cyclopentanone containing 0.1% 4-pentenal were irradiated at either 25°C or 120°C for 66 hours. An unirradiated (blank) sample was stored at each temperature for an equal time

period before analysis. Destruction of 50% of the pentenal occurred in the heated blank, whereas the pentenal was unaffected in the 25° blank. Irradiation at room temperature caused about a 32% reduction in the concentration of the aldehyde. A combination of heat and irradiation caused a 93% reduction in the pentenal concentration. It therefore appears that the effects of high temperature and irradiation are almost additive since limits of ± 5% are associated with each value.

Analyses of the gaseous products from similarly treated 4-pentenal/cyclopentanone samples showed that the destruction of the 4-pentenal in the hot blank did not result in the formation of carbon monoxide. Irradiation at room temperature and at 120° did result in increased yields of carbon monoxide, however, which suggests that there is more than one mechanism of decomposition of 4-pentenal.

(4) New products from oxygen-containing samples

A number of additional GC peaks were observed when aliquots of the room temperature ketone/oxygen samples were analyzed on the Apiezon L and Silicone grease columns. The identities of two of these products were found to be cyclopentane-1,2-dione and n-valeric acid. Analyses of gaseous products were performed on all

but one of these samples prior to the liquid product analyses. This procedure necessitated a vacuum distillation which resulted in an incomplete recovery of the slightly volatile products. No such difficulties were encountered in the recovery of the C_5 products. One liquid phase cyclopentanone/oxygen sample ($\epsilon_{O_2} = 2.37 \times 10^{-4}$) was analyzed for liquid products only, and the C_5 yields obtained from it agree reasonably well with those obtained from the distillates of the other samples (see Fig. III 12 and Tables III 35 and 36). No cyclopentanone dimers were produced in this sample which gave G values for cyclopentane-1,2-dione and n-valeric acid of 1.5 and 0.7 respectively. Varying quantities of these two products were observed in all oxygen containing samples.

Several liquid phase cyclopentanone samples which were heated to 120°C gave large GC peaks in the dimer region without irradiation. A large percentage of these "dimers" were either destroyed or not formed upon radiolysis.

A large quantity of a dark colored, viscous residue was observed on the interior walls of the vapor phase bulbs after radiolysis.

IV. DISCUSSION

A. General

The initial yields of the major products of the gamma radiolysis of cyclopentanone which were determined in this study are presented in Table IV 1. This table also includes the previously reported G values for these products (Katayama and Trumbore, 1964 and Bristowe et al., 1964), together with the yields of the analogous compounds from cyclohexanone (Singh and Freeman, 1964a). Table IV 2 contains a comparison of the yields of the minor ($G \leq 0.1$) gaseous products reported by Bristowe et al. (1964) with those found in the present study.

B. Products Involving C-H Bond Cleavage

This and subsequent sections will be devoted to a consideration of some of the more probable mechanisms of product formation. Although no definite conclusions are possible, certain mechanisms appear to be favored.

1. Hydrogen

The hydrogen yield from pure cyclopentanone (Fig. III 1A shows a slight decrease from the initial G value of 0.78 ± 0.06 with increasing dose. This decrease (calculated by least squares) may not be real and a non-variant yield of 0.75 ± 0.06 is more compatible with the constant yield of carbon monoxide since the total yield of hydrogen and carbon monoxide, determined by pressure-volume measurements

TABLE IV 1

A Comparison of the Initial Yields of the Major Products from the Radiolysis of Cyclopentanone and Cyclohexanone.

Product	G_i		
	1	2	3
Hydrogen	0.75 ± 0.06	0.68 ± 0.05	0.76 ± 0.02
Carbon monoxide	0.68 ± 0.06	1.2 - 1.5	0.48 ± 0.02
Ethylene	0.80 ± 0.04	0.85	0.12 ± 0.03
Enone	0.09 ± 0.04	0.21	0.4 ± 0.2
Alcohol	0.84 ± 0.15	0.81	0.5 ± 0.2
Enal	0.84 ± 0.10	0.74	0.85 ± 0.15
Total dimer	1.0 ± 0.1	4.4*	1.2 ± 0.4
Polymer*	1.9 ± 0.3		1.8 ± 0.3

1: Values found in the present study of cyclopentanone.

2: Values reported for cyclopentanone by Bristowe et al. (1964) and Katayama and Trumbore (1964).

3: Values reported for cyclohexanone by Singh and Freeman (1964a).

* Reported in units of monomer reacted to form polymer (excluding dimer).

TABLE IV 2

Yields of Minor Products Arising from the C-C Bond Cleavage of Cyclopentanone.

Product	1	2
Methane	<0.005	-
Ethane	~ 0.007	-
Acetylene	0.020 ± 0.004	-
Propylene	0.011 ± 0.003	-
n-Butane	0.028 ± 0.010	0.050
1-Butene	0.047 ± 0.010	0.073
Cyclobutane	0.060 ± 0.010	0.11
Methylcyclobutane	0.007 ± 0.002	-

1: G values found in the present study at a dose of 1×10^{20} eV/ml (3.2×10^{-4} eV/e^-).

2: Initial yields reported for cyclopentanone by Bristowe et al. (1964).

was independent of dose. Katayama and Trumbore (1964) also report a constant hydrogen yield, but their G value (0.68 ± 0.05) is lower than that reported here. This difference might be due to the different analytical techniques employed, but it could not be caused by the slightly higher blank value for 4-pentenal in the ketone which they radiolyzed, since no significant change in G (hydrogen) upon addition of 0.1% of 4-pentenal to the ketone was found in the present study.

The radiolytic yield of hydrogen from cyclopentanone is reduced by both benzene and 1,3-pentadiene (Fig. III 3). This reduction may be due to a scavenging mechanism involving the precursor(s) of molecular hydrogen (e.g. H atoms), or it might be due to an activation transfer process which reduces the amount of decomposition of the ketone, or it might result from a combination of the two. Several mechanisms can lead to the same type of rate equation and it is therefore convenient to classify mechanisms according to the type of rate equations which they obey. Scavenging - type mechanisms, whether they involve H atoms, positive charges, or electrons, entail a competition between two second order reactions. These mechanisms involve the reaction of the activated species with either the solute or the solvent. Activation transfer - type mechanisms involve a competition between the first order decomposition of the activated

species and the second order reaction of this species with the solute. Inherent in the following treatments is the assumption that the radiolytic hydrogen yield from each component of the binary mixture would be proportional to its electron fraction in the solution if the presence of each compound had no effect upon the radiolysis of the other.

Mechanism 1 (Scavenging Type)

$$C_5H_8O \xrightarrow{I_1} C_5H_8O^* \qquad (1)$$

$$C_5H_8O^* \longrightarrow H + (C_5H_7O)\cdot \qquad (2)$$

$$H + C_5H_8O \longrightarrow H_2 + (C_5H_7O)\cdot \qquad (3)$$

$$H + C_5H_8O \longrightarrow (C_5H_8OH)\cdot \qquad (4)$$

$$H + In \longrightarrow (HIn)\cdot \qquad (5)$$

$$H + In \longrightarrow H_2 + R_1\cdot \qquad (6)$$

The inhibitor (benzene or 1,3-pentadiene in this study) is represented by In. The radical formed by the abstraction of a hydrogen atom from the inhibitor is represented by $R_1\cdot$.

The rate of formation of $C_5H_8O^*$ is given by I_1, which is assumed to be proportional to the electron fraction of cyclopentanone in the samples studied, (ϵ_c), and $G(C_5H_8O^*) = AI_1$, where A is the constant of proportionality

which includes the irradiation dose rate.

The usual steady state treatment of Mechanism 1 leads to expressions IV-1 - IV-3.

$$\frac{d\left[H\right]}{dt} = k_2\left[C_5H_8O^*\right] - (k_3 + k_4)\left[H\right]\left[C_5H_8O\right] - (k_5 + k_6)\left[H\right]\left[In\right] = 0 \qquad \text{(IV-1)}$$

$$\frac{d\left[C_5H_8O^*\right]}{dt} = I_1 - k_2\left[C_5H_8O^*\right] = 0 \qquad \text{(IV-2)}$$

$$\frac{d\left[H_2\right]}{dt} = k_3\left[H\right]\left[C_5H_8O\right] + k_6\left[H\right]\left[In\right] \qquad \text{(IV-3)}$$

Solution of these equations leads to expression IV-4.

$$\frac{d\left[H_2\right]}{dt} = \frac{k_3 I_1}{k_3 + k_4}\left\{1 + \frac{k_6\left[In\right]}{k_3\left[C_5H_8O\right]}\Big/1 + \frac{(k_5 + k_6)\left[In\right]}{(k_3 + k_4)\left[C_5H_8O\right]}\right\} \qquad \text{(IV-4)}$$

Expression IV-4 can be rearranged to IV-5.

$$\left\{1 + \frac{k_6\left[In\right]}{k_3\left[C_5H_8O\right]}\right\}\frac{k_3/(k_3 + k_4)\, I_1}{d\left[H_2\right]/dt} = 1 + \frac{(k_5 + k_6)\left[In\right]}{(k_3 + k_4)\left[C_5H_8O\right]} \qquad \text{(IV-5)}$$

Expression IV-5 may be written in a more simplified form.

$$\left[1 + y\,(MR)\right]\rho = 1 + z\,(MR) \qquad \text{(IV-6)}$$

where $\rho = \left(\frac{k_3}{k_3 + k_4}\right) I_1 \Big/ \frac{d\left[H_2\right]}{dt}$

$$y = k_6/k_3; \quad z = \frac{k_5 + k_6}{k_3 + k_4}; \text{ and } MR = \frac{[In]}{[C_5H_8O]}$$

for Mechanism 1.

The experimental hydrogen yields can be related to ρ as follows. From an examination of steps (1) to (4) of Mechanism 1 it can be seen that

$$G_i(H_2) = \frac{k_3}{k_3 + k_4} G [C_5H_8O^*] = \frac{k_3}{k_3 + k_4} AI_1 = 0.75$$

Therefore, for the cyclopentanone solutions

$$G_{ex}(H_2)_c = \frac{k_3}{k_3 + k_4} AI_1 = 0.75 \epsilon_c \qquad \text{(IV-7)}$$

The observed yield of hydrogen from solutions is related to the rate of formation $d[H_2]/dt$ by expression IV-8.

$$G_{obs}(H_2) = A \frac{d[H_2]}{dt} + G_{In}(H_2) \epsilon_{In} \qquad \text{(IV-8)}$$

where $G_{In}(H_2)$ = $G(H_2)$ from pure inhibitor and ϵ_{In} = electron fraction of the inhibitor. ρ from expression IV-6 is given by expression IV-9.

$$\rho = \frac{G_{ex}(H_2)_c}{G_{obs}(H_2) - G_{In}(H_2) \epsilon_{In}} \qquad \text{(IV-9)}$$

Expression IV-6 can therefore be written as

$$[1 + y(MR)] \left\{ \frac{G_{ex}(H_2)_c}{G_{obs}(H_2) - G_{In}(H_2) \epsilon_{In}} \right\} = 1 + z(MR) \qquad \text{(IV-10)}$$

If Mechanism 1 is applicable, the choice of a suitable value for the parameter, y, should produce a straight line with an intercept of unity when the left-hand side of IV-10 is plotted against MR.

Several plots were made by substituting values of y from 0-5 into expression IV-10 in an attempt to produce a straight line with an intercept of unity.

Several other mechanisms considered in this study gave rise to similar expressions of MR and one of these (Mechanism 4) which involves scavenging of positive ions by the inhibitor will be presented in the appendix.

a. Benzene Solutions

The best straight line obtained when Mechanism 1 was applied to benzene/cyclopentanone solutions is shown in Fig. IV 1 which was constructed from the data given in Table IV 3. The values obtained for the parameters were $y = 1$ and $z = 2$. These values indicate that for Mechanism 1: (1) the overall rate constant for the reaction of the scavengeable species with benzene is twice as great as the overall rate constant for the reaction of this species with cyclopentanone $\left[\underline{i}.\underline{e}.\ k_5 + k_6 = 2(k_3 + k_4)\right]$ and (2) the rate constants for hydrogen atom abstraction from benzene and cyclopentanone are equal ($\underline{i}.\underline{e}.\ k_3 = k_6$). This second conclusion indicates that Mechanism 1 is inapplicable to the benzene/cyclopentanone system. Since the C-H bond dissociation energy of cyclopentanone is $\leq$ 94 kcal/mole

FIGURE IV 1

Kinetic Plot for Scavenging-Type Mechanism (Mechanism 1 or 4) for Cyclopentanone/Benzene Solutions.

$$M.R. = \frac{[\text{Benzene}]}{[\text{Cyclopentanone}]}$$

$$R_1 = [1 + M.R.] \frac{G_{ex}(H_2)_c}{G_{obs}(H_2) - G_{In}(H_2)\epsilon_{In}}$$

● : Dose rate = 0.66 ± 0.03 (10^{-5} eV/e^- hr)

○ : Dose rate = 17.3 ± 0.2 (10^{-5} eV/e^- hr)

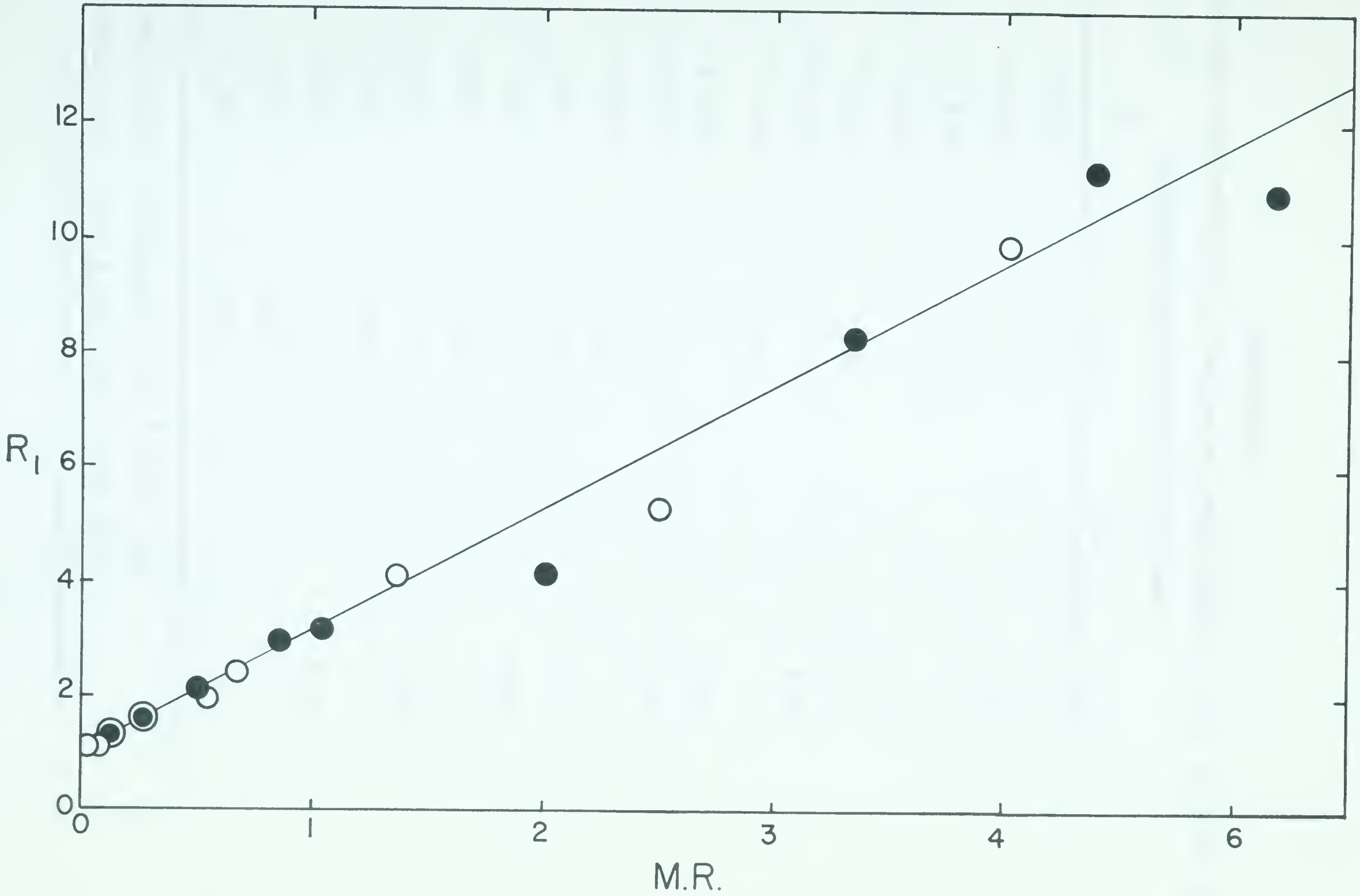

12
10
8
6
4
2
0
R_1
0
1
2
3
4
6
M.R.

TABLE IV 3

Data for Scavenging-Type Mechanism (Mechanism 1 or 4) Applied to Cyclopentanone/Benzene Solutions.

MR	R_1	
	A	B
0.023	-	1.12
0.063	-	1.16
0.122	1.34	-
0.123	-	1.34
0.263	1.64	-
0.264	-	1.66
0.498	2.15	-
0.528	-	2.00
0.664	-	2.42
0.850	3.01	-
1.03	3.15	-
1.36	-	4.10
2.00	4.14	-
2.54	-	5.28
3.35	8.31	-
4.02	-	9.90
4.39	11.2	-
5.18	10.8	-

A: Dose rate = 0.66 ± 0.03 (10^{-5} eV/e^- hr)

B: Dose rate = 17.3 ± 0.2 (10^{-5} eV/e^- hr)

[since D(iso-C_3H_7-H) $\approx$ 94 kcal/mole] and D(C_6H_5-H) is about 102 kcal/mole (Cottrell, 1958) it seems probable that k_6 would be less than k_3.

For Mechanism 4 (Appendix) values of y = 1 and z = 2 indicate that: (1) the rate constant for the reaction of a ketone molecular ion with benzene is twice as large as the rate constant for the ion with a ketone molecule and (2) one-half of the benzene ions produced by positive charge scavenging reactions result in the formation of hydrogen. The ionization potential of cyclopentanone (9.26 eV) is approximately the same as that of benzene (9.25 eV) (Watanabe et al., 1962). It is therefore possible that a transfer of positive charge from cyclopentanone to benzene could occur (reaction 21, Mechanism 4, Appendix). It would seem unlikely, however, that one-half of the positively charged benzene ions would produce hydrogen because of the low hydrogen yield (G = 0.038) from pure benzene. It therefore appears that Mechanism 4 is also inapplicable to the benzene/cyclopentanone solutions.

b. 1,3-Pentadiene Solutions

The lack of precision of the hydrogen yields from 1,3-pentadiene/cyclopentanone solutions prevented a meaningful conclusion from being drawn from the kinetic analysis of the results.

Mechanism 2 (Activation Transfer)

$$C_5H_8O \xrightarrow{I_2} C_5H_8O^* \qquad (7)$$

$$C_5H_8O^* \longrightarrow (C^*) \longrightarrow H_2 + \text{residue} \qquad (8)$$

$$C_5H_8O^* + In \longrightarrow C_5H_8O + In^* \qquad (9)$$

$$In^* \longrightarrow (C^*) \longrightarrow H_2 + \text{residue} \qquad (10)$$

$$In^* \longrightarrow In \qquad (11)$$

where (C*) could be an hot (i.e. unscavengeable) hydrogen atom or some type of activated complex which decays to form molecular hydrogen. Reactions 8 and 10 could each involve more than one molecule and both reactions may involve more than one step. The meanings of the other symbols are similar to those in Mechanism 1.

Application of the usual steady state treatment to Mechanism 2 gives rise to expression IV-11.

$$(1 + v\,[In])\,\rho = 1 + u\,[In] \qquad (IV\text{-}11)$$

when $v = \dfrac{k_9 k_{10}}{k_8(k_{10} + k_{11})}$; $u = k_9/k_8$; and

$$\rho = \frac{I_2}{d\,[H_2]\,/dt} = \frac{G_{ex}(H_2)_c}{G_{obs}(H_2) - G_{In}(H_2)\,\epsilon_{In}}$$

for Mechanism 2.

Substitution of arbitrary integral values of v into expression IV-11 was followed by the construction of plots

of the left-hand side of equation IV-11 against the concentration of the inhibitor. This treatment should produce a straight line with an intercept of unity.

Mechanism 5 in the Appendix gives rise to an expression of the same form as IV-11.

The best straight line obtained when Mechanism 2 was applied to the hydrogen yields from the benzene/cyclopentanone solutions is shown in Fig. IV 2. The data used in constructing this figure are presented in Table IV 4. This line was obtained from v = 0 and the slope corresponds to a value of u = 0.1 liters/mole. This value of v indicates that benzene does not produce hydrogen following activation transfer from the ketone (Mechanisms 2 and 5). This conclusion is similar to that reached previously for benzene/cyclohexanone solutions (Singh, 1963). The value of u = 0.1 liters/mole is also similar to that reported for cyclohexanone (0.2 liters/mole), thereby indicating that the mechanisms of hydrogen formation in the two systems are somewhat alike.

Mechanism 3 (A Dose Rate Dependent Scavenging Mechanism)

An example of a reaction mechanism which predicts that the degree of inhibition of hydrogen formation in solutions should depend upon the dose rate is the following charge-scavenging mechanism.

$$C_5H_8O \xrightarrow{I_3} M^+ + N^- \qquad (12)$$

FIGURE IV 2

Kinetic Plot for Activation Transfer - Type Mechanism (Mechanism 2 or 5) for Cyclopentanone/Benzene Solutions.

$$\rho = \frac{G_{ex}(H_2)_c}{G_{obs}(H_2) - G_{In}(H_2)\epsilon_{In}}$$

----- = Values of ρ predicted by Mechanism 3 for low dose rate cyclopentanone/benzene solutions.

● : Dose rate = 0.66 ± 0.03 (10^{-5} eV/e$^-$ hr)

○ : Dose rate = 17.3 ± 0.2 (10^{-5} eV/e$^-$ hr)

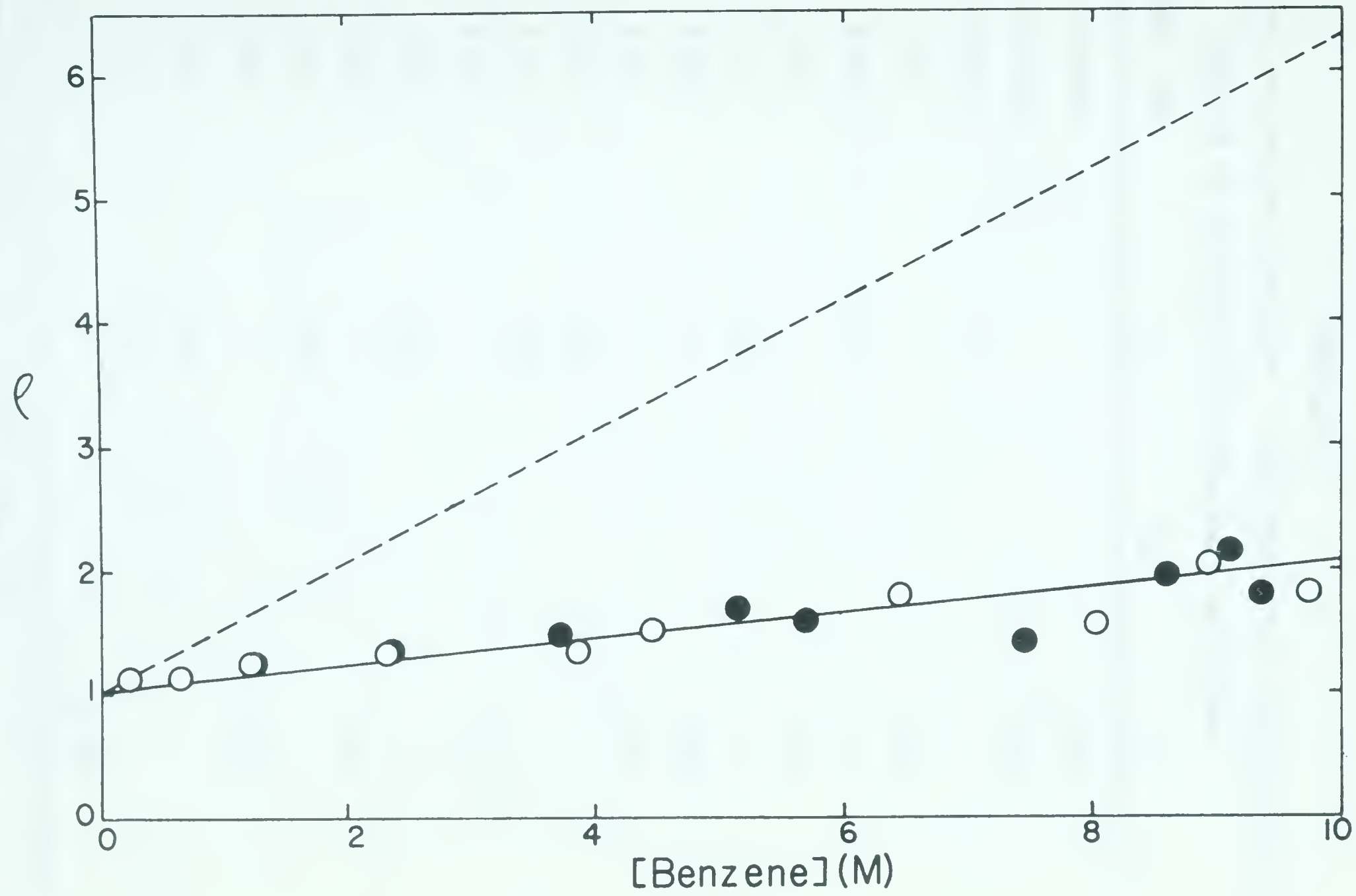

ρ
0
1
2
3
4
5
6
0
2
4
6
8
10
[Benzene](M)

TABLE IV 4

Data for Activation Transfer - Type Mechanism (Mechanism 2 or 5) Applied to Cyclopentanone/Benzene Solutions.

Benzene (M)	R_2	
	A	B
0.255	-	1.13
0.559	-	1.12
1.22	1.23	-
1.23	-	1.22
2.33	1.33	-
2.34	-	1.34
3.73	1.48	-
3.87	-	1.34
4.47	-	1.49
5.14	1.67	-
5.69	1.59	-
6.46	-	1.78
7.46	1.41	-
8.04	-	1.53
8.61	1.96	-
8.96	-	2.02
9.10	2.13	-
9.38	1.80	-
9.75	-	1.80

A: Dose rate = 0.66 ± 0.03 (10^{-5} eV/e^- hr)

B: Dose rate = 17.3 ± 0.2 (10^{-5} eV/e^- hr)

$$M^+ + N^- \longrightarrow H_2 + P \qquad (13)$$

$$M^+ + In \longrightarrow M + In^+ \qquad (14)$$

$$In^+ + N^- \longrightarrow Q \qquad (15)$$

where In is the inhibitor and P and Q are products other than hydrogen. The inhibitor kinetics would not be changed if reaction (12) were written in several steps *e.g.*

$$C_5H_8O \rightsquigarrow C_5H_8O^+ + e^-$$

$$e^- + C_5H_8O \longrightarrow C_5H_8O^-$$

$$C_5H_8O^+ + C_5H_8O \longrightarrow C_5H_8OH^+ + (C_5H_7O)\cdot$$

For purposes of testing this mechanism the identities of M^+ and N^- do not matter, except that N^- is probably not a free electron. Thus $k_{13} \approx k_{15}$. Steady state treatment of this mechanism leads to:

$$\frac{d\left[H_2\right]}{dt} = \frac{(k_{13}I_3)^{\frac{1}{2}} I_3}{(k_{13}I_3)^{\frac{1}{2}} + k_{14}\left[In\right]} \qquad (IV\text{-}12)$$

or:

$$\frac{I_3}{d\left[H_2\right]/dt} = 1 + \frac{k_{14}\left[In\right]}{(k_{13}I_3)^{\frac{1}{2}}} = \rho \qquad (IV\text{-}13)$$

where ρ has the same meaning as in Mechanisms 1 and 2.

Since the dielectric constant of cyclopentanone is about 14 (see footnote page 6), the yield of 'free ions' is probably large enough to make this mechanism a reasonable possibility.

The values of ρ obtained for benzene solutions at two dose rates which differ by a factor of 26 are plotted vs. [In] in Fig. IV 2 and listed in Table IV 4. It is evident from this figure that the degree of inhibition obtained by a given benzene concentration is independent of the dose rate, so the ionic mechanism outlined above which would indicate that solutions irradiated at the lower dose rate should fall on the dashed line, does not apply.

This work also rules out other mechanisms which involve homogeneous competition between reactions of the type

$$2\ X \longrightarrow H_2 + P$$

$$X + In \longrightarrow Q$$

where X is any precursor of hydrogen.

The simple activation transfer mechanism (Mechanism 2) provides the best explanation (of any mechanism tried) of the results from benzene/cyclopentanone solutions.

In conclusion it appears that benzene inhibits the formation of hydrogen primarily by interfering with the precursor(s) of hydrogen (other than hydrogen atoms).

It might be noted that a molecular elimination process does not make a large contribution to the hydrogen yield since G (hydrogen) is 0.75 and G (cyclopentenone) is 0.09 and it is likely that some of the cyclopentenone is formed by disproportionation of $C_5H_7O\cdot$ radicals.

2. Cyclopentanol

The constantly decreasing yield of cyclopentanol with increasing dose (Fig. III 1B) is probably due to secondary reactions. The agreement between the initial yield of the alcohol reported by Bristowe et al. (1964), (0.81), and that found in the present study (0.84 ± 0.15) might be fortuitous when one considers the limits placed on this value in the present study. In addition, Bristowe et al. (1964) found that the alcohol yield did not decrease with dose until the absorbed dose was about 2×10^{20} eV/ml. The reason for this difference in dose effect is not apparent.

Cyclopentanol is probably formed by abstraction and disproportionation reactions of the $C_5H_9O\cdot$ radical as shown in equations IV-14 and IV-15.

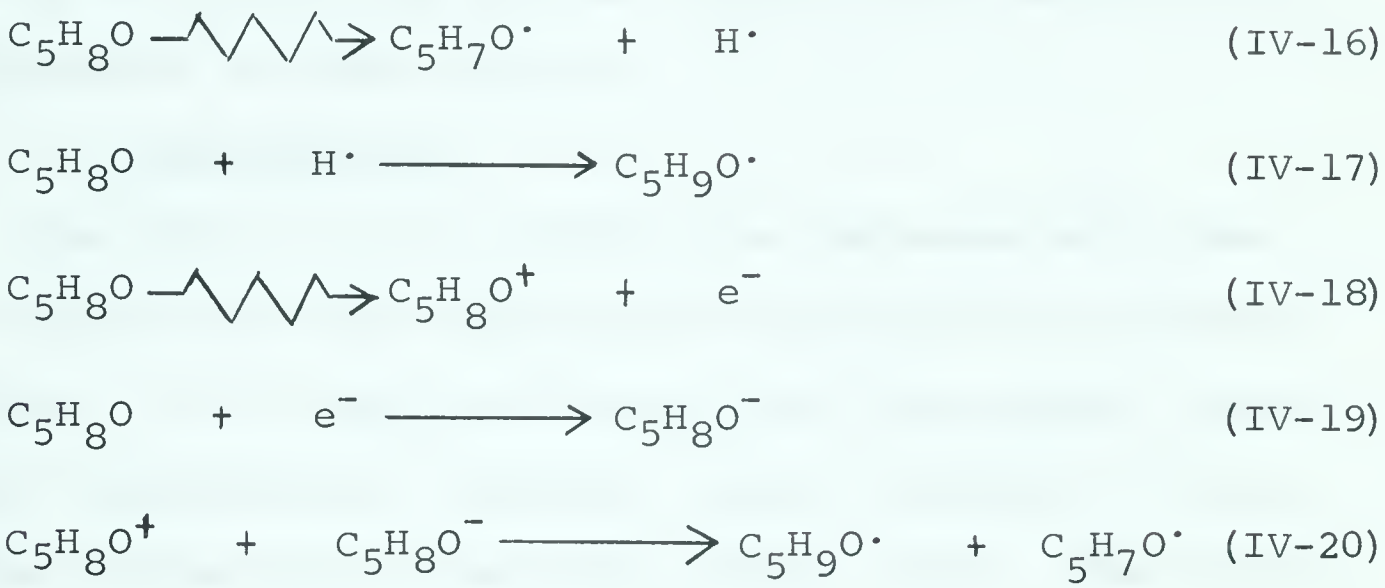
$$C_5H_9O\cdot + C_5H_8O \longrightarrow C_5H_9OH + C_5H_7O\cdot \quad \text{(IV-14)}$$

$$2\ C_5H_9O\cdot \longrightarrow C_5H_9OH + C_5H_8O \quad \text{(IV-15)}$$

This radical was recently cited as the source for cyclopentanol (Bristowe et al., 1964) and the analogous radical was

suggested as the precursor for cyclohexanol in the cyclohexanone system (Singh and Freeman, 1964b).

Two modes of formation of the $C_5H_9O\cdot$ radical are given in equations IV-16 to IV-20.



$$C_5H_8O \xrightarrow{\sim\sim} C_5H_7O\cdot + H\cdot \qquad \text{(IV-16)}$$

$$C_5H_8O + H\cdot \longrightarrow C_5H_9O\cdot \qquad \text{(IV-17)}$$

$$C_5H_8O \xrightarrow{\sim\sim} C_5H_8O^+ + e^- \qquad \text{(IV-18)}$$

$$C_5H_8O + e^- \longrightarrow C_5H_8O^- \qquad \text{(IV-19)}$$

$$C_5H_8O^+ + C_5H_8O^- \longrightarrow C_5H_9O\cdot + C_5H_7O\cdot \qquad \text{(IV-20)}$$

The addition of hydrogen atoms to ketones in radiolytic systems has been suggested by numerous workers (e.g. Strong and Burr, 1959; Hardwick, 1962; Singh and Freeman, 1964b; and Bristowe et al., 1964). The possible forms of the analogous radical in the cyclohexanone system ($C_6H_{11}O\cdot$) were shown earlier (equation I-36). As previously discussed by Singh (1963), the concentration of a particular isomer depends upon its mode of formation.

The rapid disappearance of cyclopentanol as a radiolytic product from solutions containing pentadiene (Fig. III 4A and B) is in sharp contrast to the effect on the alcohol yield caused by benzene (Fig. III 4B). This is consistent with the relative scavenging abilities of

the two additives (Levy and Szwarc, 1954 and Rajbenbach and Szwarc, 1959). Pentadiene probably reduces the alcohol yield by scavenging the $C_5H_9O^{\cdot}$ radicals. The similar reductions of the hydrogen and alcohol yields by benzene (Fig. III 3B and III 4B) may be caused by the deactivation of a precursor of both products.

3. Cyclopentenone

The yield of this product also decreased with dose (Fig. III 1B) and this decrease is attributed to secondary reactions. It is possible that some of this product could undergo a dimerization reaction. Such a reaction is known to occur in photolytic reactions (Eaton, 1962). The initial yield (0.09) was obtained by a linear extrapolation of the results to zero dose. Bristowe et al. (1964) found that the cyclopentenone yield decreased only at doses greater than 10^{20} eV/ml. The analytical instruments which they used enabled them to measure the yield of this compound at lower doses than those possible in the present study, so their initial yield (0.21) might be the more accurate.

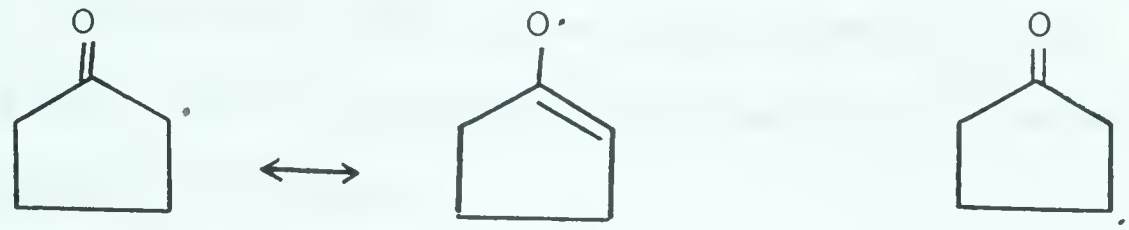
Three possible mechanisms for the formation of cyclopentenone are shown in equations IV-21 to IV-23.

$$C_5H_8O \rightsquigarrow C_5H_6O + H_2 \qquad \text{(IV-21)}$$

$$C_5H_7O^{\cdot} + R^{\cdot} \longrightarrow C_5H_6O + RH \qquad \text{(IV-22)}$$

$$2\ C_5H_7O^{\cdot} \longrightarrow C_5H_6O + C_5H_8O \qquad \text{(IV-23)}$$

where R· is any free radical other than C_5H_7O·. The formation of the C_5H_7O· radical may result from reactions IV-16 and IV-20. This mechanism is similar to that postulated previously for the formation of cyclohexenone from cyclohexanone (Singh, 1963). Two possible structures of the C_5H_7O· radical are I and II.



I II

Disproportionation of I would result in the formation of 2-cyclopentenone, while II could give rise to either 2- or 3-cyclopentenone. The decreased yield of cyclopentenone with increasing dose could be due to reaction IV-24, where R· is any free radical.

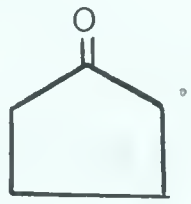
$$C_5H_6O + R\cdot \longrightarrow (R\text{-}C_5H_6O)\cdot \qquad \text{(IV-24)}$$

Since Rajbenbach and Szwarc (1959) have shown that conjugated dienes are much better radical scavengers than isolated dienes, it is likely that the yield of 2-cyclopentenone would be reduced more rapidly than that of 3-cyclopentenone.

4. Dimers

The yield of total " dimers" increases slightly over the region studied (Fig. III 2A). Bristowe et al.

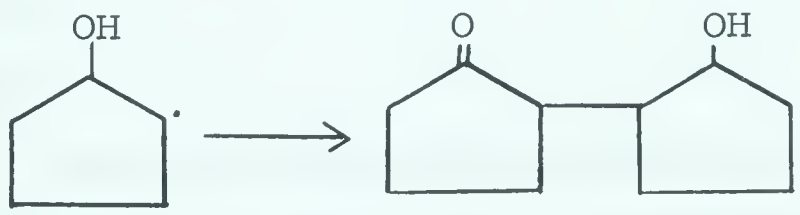
(1964) reported that the yield of dimers, in arbitrary units, increased markedly in the region 1.5 - 2.5 x 10^{20} eV/ml, but this reported behavior is based largely on one point and was not found in the present study. Formation of the ketone dimers is probably due to radical combination reactions. Bicyclopentyl-2,2'-dione (BCD) accounted for about 70% of the total dimer yield found in the present study, thus indicating the presence of radical III in the radiolytic system.



III

2 III $\longrightarrow$ BCD (IV-25)

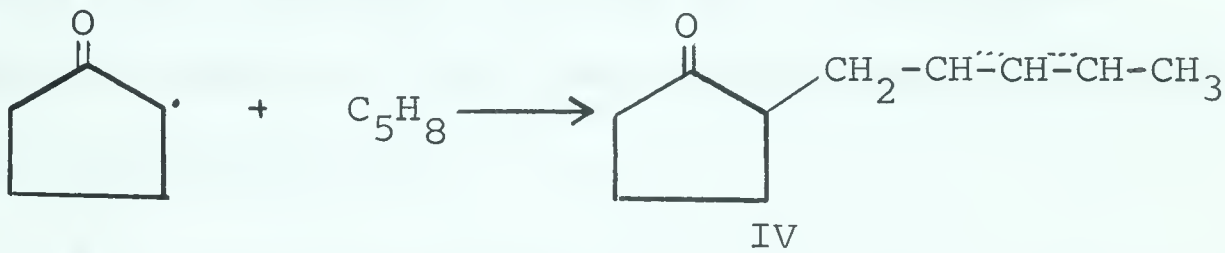
This equation (IV-25) was recently cited as that responsible for dimer formation in the radiolysis of cyclopentanone (Bristowe et al., 1964). Other dimers probably result largely from the reactions of III with other radicals (e.g. equation IV-26).



III + (IV-26)

The addition of small quantities of 1,3-pentadiene or oxygen sharply reduces the yield of the dimeric products, while the addition of benzene causes a much more gradual

decrease (Fig. III 5B and C). Conjugated dienes are good radical scavengers (Rajbenbach and Szwarc, 1959) and the effect of 1,3-pentadiene on the dimer yield is therefore consistent with a free radical mechanism for dimer formation. This mechanism is substantiated by the effect of oxygen which is also known to act as a radical scavenger (Schuler, 1958). Equation IV-27 shows a typical scavenging reaction by the diene which would prevent the formation of BCD.



(IV-27)

IV

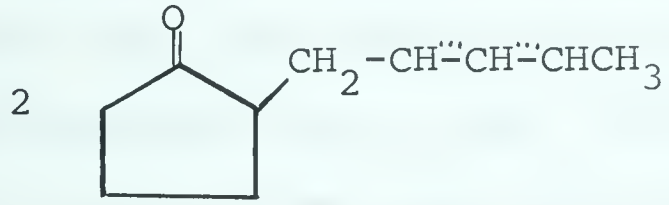
The small amount of inhibition of dimer formation by benzene is probably due to an activation transfer process which prevents formation of the necessary radicals since benzene is known to be a poor radical scavenger (Levy and Szwarc, 1954). These conclusions are in accord with those reached earlier for the cyclohexanone system (Singh and Freeman, 1964b).

5. Polymer

The initial yield of chloroform soluble polymer (excluding dimer and reported in units of monomer incorporated into polymer) is 1.9 $\pm$ 0.3. The yield increases with increasing dose as shown in Fig. III 2B.

The initial yield of all polymeric species, including dimers, in these same units is 3.9 ± 0.5. It is therefore likely that the polymer yield of 4.4 (at a dose of 1 x 10^{19} eV/ml) reported by Bristowe et al. (1964) includes dimer. If changes in the polymer composition from pure cyclopentanone did occur with increasing dose, they were too small to be detected by microanalysis and no definite deviation from $(C_5H_8O)_n$ could be found.

The polymer obtained from cyclopentanone solutions containing 0.003 electron fraction of 1,3-pentadiene corresponded closely to the dimer of IV (equation IV-28) as shown in Table III 16.



(IV-28)

IV

Radicals other than III (page 186), produced from cyclopentanone, were doubtless also included in this polymer. The analysis of the polymer indicated that it contained all of the pentadiene which had reacted during radiolysis, so allylic radicals such as IV do not disproportionate to any appreciable extent.

The total polymer yield increased with increasing concentration of 1,3-pentadiene reaching a maximum of G (polymer) = 25 (in C_5 units) for pure pentadiene (Fig. III 6

and Table III 15). Fig. III 6 represents the yield of $C_{20}H_{30}O_2$ together with the polymer produced by reaction IV-29.

$$n \quad C_5H_8 \longrightarrow (C_5H_8)_n \qquad \text{(IV-29)}$$

The data in Table III 15 indicate the increasing contribution of reaction IV-15 to the total polymer yield with increasing diene concentration.

B. Products Arising from C-C Bond Cleavage

1. Results from Pure Cyclopentanone

a. Carbon Monoxide

The radiolytic yield of carbon monoxide from pure cyclopentanone found in the present study (G_i = 0.68) is larger than that obtained by Singh and Freeman (1964a) from cyclohexanone (G_i = 0.48). The lowest doses used in these two investigations were about the same ($\sim 5 \times 10^{18}$ eV/g) and both studies indicated that the yield of this product was independent of dose. Katayama and Trumbore (1964) have recently reported a much higher yield of carbon monoxide from cyclopentanone (1.5 $\pm$ 0.3). They reported that the yield decreased with increasing dose until attaining a constant value of 0.7 at doses $> 10^{20}$ eV/g. The difference between the yield of carbon monoxide from cyclopentanone reported by Katayama and Trumbore (1964) and that found in the present study might result from the difference in the

gas analysis techniques. If the first point in their curve of dose against yield (in moles) for carbon monoxide (Fig. I, Katayama and Trumbore, 1964) were ignored, the other points fall reasonably well on a straight line which extrapolates to an intercept of 0.25 μmoles. This line would correspond to G (carbon monoxide) = 0.68.

b. Ethylene

The yield of ethylene found in the present study (G = 0.80 ± 0.04) agrees well with that reported by Bristowe et al. (1964) as shown in Table IV 1. Both studies showed that the yield was independent of dose and of the presence of oxygen.

c. 4-Pentenal

The initial yield of 4-pentenal found in the present study (0.84 ± 0.10) is the same as that reported by Singh and Freeman (1964a) for 5-hexenal from the radiolysis of cyclohexanone. Both studies showed that the yields of the analogous aldehydes decreased with increasing dose. Bristowe et al. (1964) reported that the yield of 4-pentenal (G = 0.74) was unaffected by dose up to the highest dose they used (2.5×10^{20} eV/g). The fact that radiolytic destruction of the aldehyde was observed in samples which contained 0.1% of 4-pentenal supports the negative slope of the dose-yield curve shown in Fig. III 7C.

d. C_4 Products

The yields of n-butane, cyclobutane and 1-butene

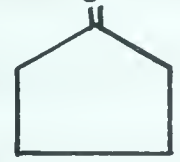
found in the present study and reported in Table IV 2 are about one-half those reported by Bristowe et al. (1964). These differences may be due to an incomplete separation of these products from the radiolyzed liquid by the vacuum line techniques used in the present study. This explanation is supported by (1) the fact that agreement was obtained in the two studies on the yield of ethylene, and (2) the fact that all three C_4 compounds have low and almost equal vapor pressures at -80°C. It is not considered likely by the present author, however, that almost 0.1 G units of gaseous products would not be recovered since all gaseous fractions were doubly distilled and the increase obtained from the second distillation seldom exceeded 0.03 G units. Third distillations, when performed, usually gave an immeasurably small additional increase. The yields of these products may therefore lie between the values obtained in the two studies and presented in Table IV 2.

2. A Consideration of Biradical Mechanisms

The data obtained in the present study do not establish whether the formation of the products occurs through a biradical process or as a result of a concerted mechanism. Since the present results are satisfactorily explained in terms of biradical intermediates, a biradical mechanism will be presented. Several investigators have postulated that the photolytic decomposition of cyclopentanone proceeds by a biradical mechanism as was mentioned earlier (Benson and

Kistiakowsky, 1942; Blacet and Miller, 1957). Srinivasan (1959a, 1959b) has studied the photoisomerization of a number of cyclic ketones (e.g. cyclopentanone) and has attributed the formation of the various unsaturated aldehydes (e.g. 4-pentenal) to a concerted process.

Flowers and Frey (1960) reported that in the presence of a high pressure of ethylene, the vapor phase photolysis of cyclopentanone gave rise to several C_6 compounds in addition to the photolysis products from pure cyclopentanone (cyclobutane, ethylene and carbon monoxide). These investigators explained the formation of the C_6 products by the reactions shown in equations IV-30 to IV-33.



$$+ \quad h\nu \longrightarrow \dot{C}H_2(CH_2)_2\dot{C}H_2 \quad + \quad CO \qquad \text{(IV-30)}$$

$$\dot{C}H_2(CH_2)_2\dot{C}H_2 \quad + \quad C_2H_4 \longrightarrow \dot{C}H_2(CH_2)_4\dot{C}H_2 \qquad \text{(IV-31)}$$

$$\dot{C}H_2(CH_2)_4\dot{C}H_2 \longrightarrow \text{cyclohexane} \qquad \text{(IV-32)}$$

$$\dot{C}H_2(CH_2)_4\dot{C}H_2 \longrightarrow \text{hexenes} \qquad \text{(IV-33)}$$

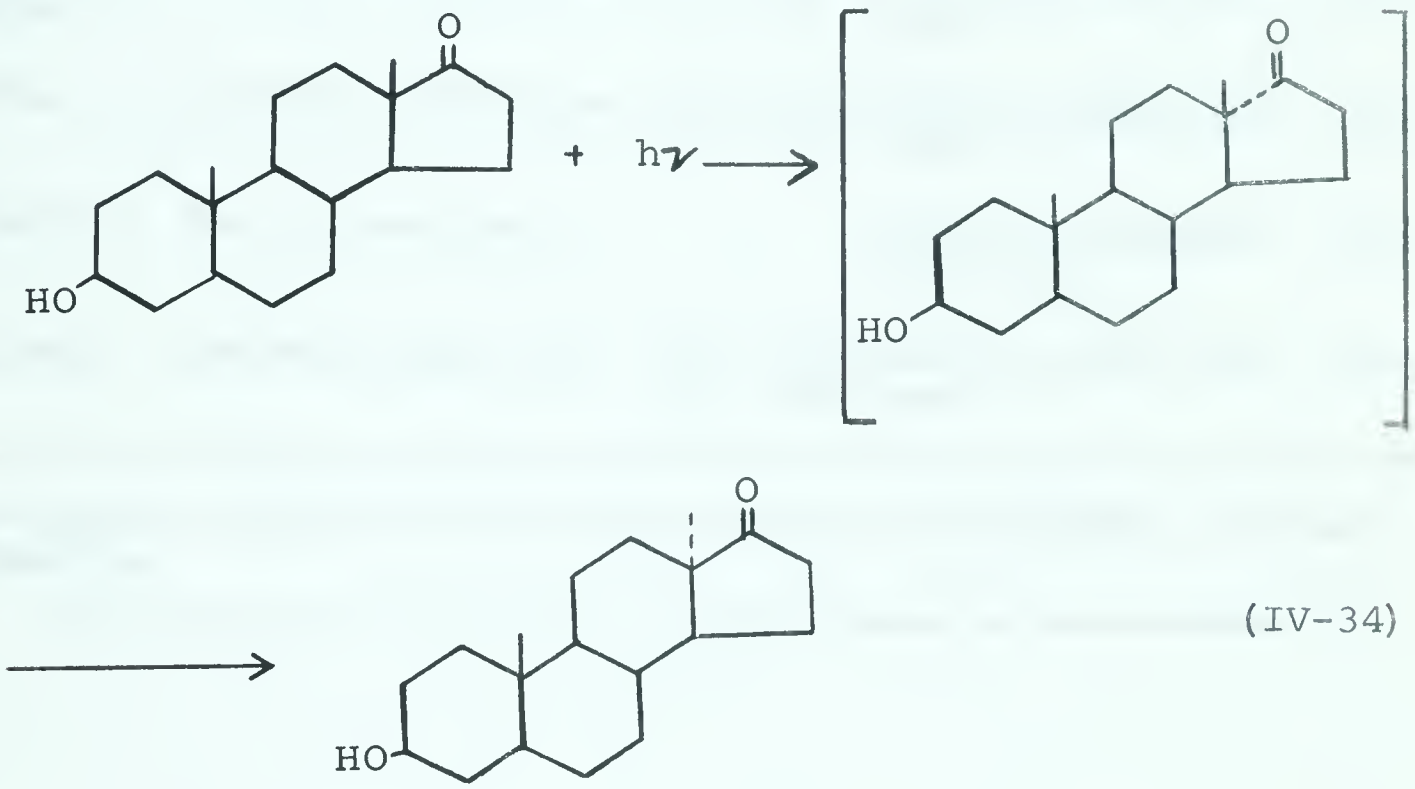
The vapor photolysis of cyclobutanone in the presence of a high pressure of ethylene was found to give a number of C_5 olefins but no cyclopentane, in addition to the photolysis products of pure cyclobutanone (Flowers and Frey, 1960). These authors suggested that the C_5 products were formed by the addition of the trimethylene biradical to ethylene to

yield a pentamethylene biradical which then underwent an intramolecular hydrogen atom abstraction reaction.

Srinivasan (1961a, 1961b) has since suggested that all of the photolytic products from cyclopentanone arise by concerted processes. In a recent review of the photolyses of cyclic ketones, Srinivasan (1963) pointed out that few experimental details of the photolytic work on cyclopentanone - ethylene mixtures were reported. Srinivasan (1963) also suggested that since the total quantum yield for the decomposition of cyclopentanone was independent of the presence of a variety of foreign gases, the effects of added ethylene (Flowers and Frey, 1960) should be checked. Srinivasan (1959a, 1959c) reported that added oxygen increased the quantum yield of 4-pentenal from cyclopentanone and 5-hexenal from cyclohexanone, and relied heavily on these data to substantiate his argument in favor of a concerted mechanism. Singh (1963) found that added oxygen inhibited the formation of 5-hexenal from the liquid phase radiolysis of cyclohexanone and further reported that oxygen reacted with the ketone even in unirradiated samples. The product of this 'dark reaction' had a retention time close to that of 5-hexenal. Srinivasan did not report any blank reaction on a similar GC column which suggests that his reported 5-hexenal sensitization by oxygen should be checked. Singh (1963) postulated a mechanism involving biradicals to explain

the radiolytic products from cyclohexanone but emphasized that a concerted mechanism could not be ruled out on the basis of his data.

An example of a reaction which very likely proceeds by a biradical mechanism is the photoisomerization of androsterone to lumiandrosterone as shown in equation IV-34 (deMayo, 1960).



(IV-34)

3. Speculation on the Energy States Involved in Product Formation

The effects of added benzene or 1,3-pentadiene on the yields of hydrogen and the radiolytic products arising from C-C bond cleavage are summarized in Table IV 5.

The data in Table IV 5 suggest that more than one excited species is responsible for the formation of these products. The possible energy levels will be discussed in

TABLE IV 5

The Effects of Additives on Yields of Hydrogen and Products Arising from C-C Bond Cleavage.

Product	1,3-Pentadiene		Benzene	
	Effect on Product	Figure	Effect on Product	Figure
Hydrogen	Marked inhibition	III 3A	Inhibition	III 3B
Carbon monoxide	Slight inhibition	III 9A	Slight sensitization	III 9B
Ethylene	Slight inhibition	III 10A	Slight sensitization	III 10B
C_4 Products	Not determined*	-	Slight sensitization (?)	III 12
4-Pentenal	Marked inhibition	III 11A, III 11B	Marked sensitization	III 11B

* Analytical difficulties prevented the measurement of these products.

order of decreasing excitation energies.

a. Hydrogen

A number of excited states may be involved in the radiolytic formation of hydrogen. For simplicity these will be designated as $C_5H_8O^{(1)}$. Added benzene may reduce the hydrogen yield by a reaction such as IV-35.

$$C_5H_8O^{(1)} + C_6H_6 \longrightarrow P_1 + P_2 \qquad \text{(IV-35)}$$

where P_1 and P_2 represent products other than hydrogen.

Hydrogen inhibition by 1,3-pentadiene is more complex, as was mentioned earlier.

b. Ethylene

The radiolytic formation of ethylene probably arises from a second group of states, $C_5H_8O^{(2)}$ which are capable of undergoing reactions IV-36 to IV-38.

$$C_5H_8O^{(2)} \longrightarrow \dot{C}H_2(CH_2)_3\dot{C}O^{**} \qquad \text{(IV-36)}$$

$$\dot{C}H_2(CH_2)_3\dot{C}O^{**} \longrightarrow \dot{C}H_2(CH_2)_2\dot{C}H_2^{*} + CO \qquad \text{(IV-37)}$$

$$\dot{C}H_2(CH_2)_2\dot{C}H_2^{*} \longrightarrow 2\ C_2H_4 \qquad \text{(IV-38)}$$

c. C_4 Products

Cyclobutane, 1-butene and n-butane probably arise from a group of states designated as $C_5H_8O^{(3)}$ which give rise to the tetramethylene biradical as shown in equations

IV-39 and IV-40.

$$C_5H_8O^{(3)} \longrightarrow \dot{C}H_2(CH_2)_3\dot{C}O^* \qquad \text{(IV-39)}$$

$$\dot{C}H_2(CH_2)_3\dot{C}O^* \longrightarrow \dot{C}H_2(CH_2)_2\dot{C}H_2 + CO \qquad \text{(IV-40)}$$

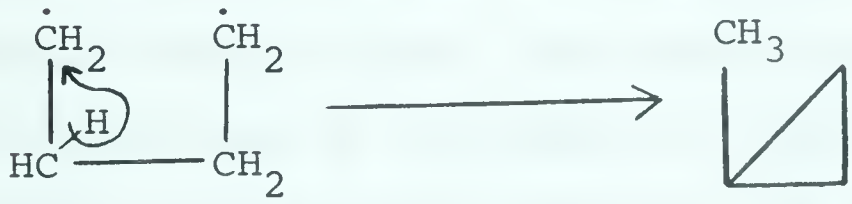
The tetramethylene biradical may rapidly close to produce cyclobutane or undergo an intramolecular hydrogen atom abstraction to produce 1-butene or methylcyclopropane or it might abstract two hydrogen atoms and form n-butane as shown in the following equations.



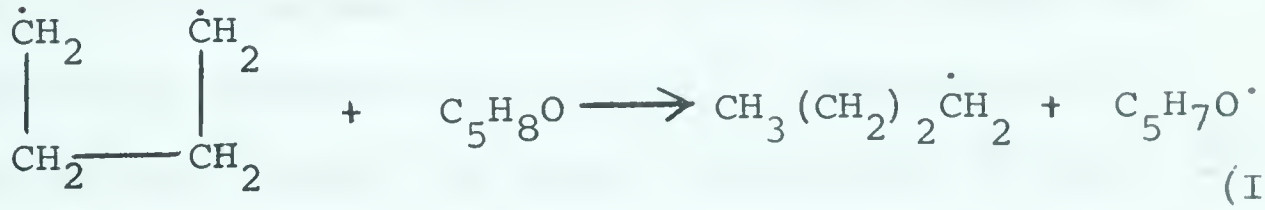
(IV-41)



(IV-42)



(IV-43)



(IV-44)

$$CH_3(CH_2)_2\dot{C}H_2 + C_5H_8O \longrightarrow n\text{-}C_4H_{10} + C_5H_7O^{\cdot} \qquad \text{(IV-45)}$$

d. 4-Pentenal

The radiation induced isomerization of cyclopentanone to 4-pentenal probably arises from yet another group of states represented by $C_5H_8O^{(4)}$ as shown in equations IV-46 and IV-47.

$$C_4H_8O^{(4)} \longrightarrow \dot{C}H_2(CH_2)_3\dot{C}O \qquad \text{(IV-46)}$$

$$\dot{C}H_2(CH_2)_3\dot{C}O \longrightarrow CH_2{=}CH_2CH_2CH_2CHO \qquad \text{(IV-47)}$$

e. Minimum Energies of the Excited States Responsible for Product Formation

Since hydrogen is the only one of the products shown in Table IV 5 which exhibits inhibition by benzene, $C_5H_8O^{(1)}$ must represent the group of states possessing the highest excitation energy since the formation of $C_5H_8O^{(1)}$ by energy transfer from an excited benzene molecule was not observed. It is therefore likely that $C_5H_8O^{(1)}$ represents a group of states which possesses a larger amount of electronic excitation energy whereas the states $C_5H_8O^{(2)}$ - $C_5H_8O^{(4)}$ might differ only in the degree of vibrational excitation.

The marked sensitization of 4-pentenal by benzene coupled with the marked inhibition of this product by 1,3-pentadiene indicate that $C_5H_8O^{(4)}$ represents the group of states having the lowest excitation energy. The data obtained on the effects of additives on the yields of carbon monoxide, ethylene and the C_4 products do not allow

one to postulate the relative energy levels of $C_5H_8O^{(2)}$ and $C_5H_8O^{(3)}$. A consideration of the relative energy requirements for reactions IV-35 to IV-47 is somewhat helpful in this respect.

Since D $[CH_3CO—CH_3]$ = 72 kcal/mole (Cottrell, 1958), reaction IV-48 would require about 72 kcal/mole.

$$C_5H_8O \longrightarrow \dot{C}H_2(CH_2)_3\dot{C}O \qquad \text{(IV-48)}$$

D $[CH_3—CO] \sim$ 17 kcal/mole (Cottrell, 1958) so that reaction IV-49 would require of the order of 17 kcal/mole.

$$\dot{C}H_2(CH_2)_3\dot{C}O \longrightarrow \dot{C}H_2CH_2CH_2\dot{C}H_2 + CO \qquad \text{(IV-49)}$$

As a first approximation, D $[CH_2CH_2—CH_2CH_2]$ may be about 5 kcal/mole (Freeman, 1964).

Thus the total minimum excitation energies of the groups of states are: $C_5H_8O^{(2)} \sim$ 95 kcal/mole, $C_5H_8O^{(3)}$ 90 kcal/mole, and $C_5H_8O^{(4)} \sim$ 70 kcal/mole. Since the second and third groups of energy states differ in excitation energy by only about 5 kcal/mole, it is not surprising that the yields of carbon monoxide and the C_2 and C_4 products show similar amounts of inhibition or sensitization as shown in Table IV 5.

It should be mentioned, however, that the amounts of inhibition or sensitization may be dependent upon the lifetimes of the species involved. In general, a longer lifetime would be associated with an increased likelihood of activation transfer processes.

4. Explanation of the Effects of Additives on Product Yields

a. 4-Pentenal

Benzene caused a marked sensitization of the formation of 4-pentenal (Fig. III 11B) whereas the yield is reduced by both oxygen (Fig. III 13A) and 1,3-pentadiene (Fig. III 11A, B). The lowest singlet and triplet excitation energies and the first ionization potentials of the compounds radiolyzed in this study are summarized in Table IV 6. Oxygen, unlike the other two additives and cyclopentanone, has a triplet ground state. Spin conservation therefore requires that the singlet levels of oxygen be compared with the triplet states of the other molecules and its triplets with the other singlets. The data in Table IV 6 indicate that activation transfer would occur in the 'proper' direction if the lowest triplet state of cyclopentanone were the precursor involved in these sensitization and inhibition reactions. The lowest excited singlet state of cyclopentanone would not transfer energy to oxygen or to pentadiene. Charge transfer would not occur between the ground state of the cyclopentanone molecular ion and oxygen.

Hammond et al. (1962) found that the photolysis of a benzene solution containing an olefin (e.g. 1,3-pentadiene) together with an aldehyde or a ketone, caused an efficient

TABLE IV 6

Lowest Singlet and Triplet Excitation Energies and Ionization Potentials (in e.V.).

Compounds	Triplet	Singlet	I.P.
Cyclopentanone	2.8[a]	4.14[b]	9.26[c]
Benzene	3.59[b]	4.76[b]	9.25[c]
1,3-Pentadiene	2.6[d]	5.4[d]	9.0[e]
Oxygen	4.35[f]	0.98[f] 1.64[f]	12.2[f]

a: La Paglia and Roquitte (1962).

b: Rao (1961).

c: Watanabe, et al. (1962).

d: Hammond, et al. (1962).

e: Obtained by comparing the ionization potentials of 1-butene, 1,3-butadiene, and 1-pentene from Watanabe, et al. (1962).

f: Herzberg (1959).

cis-trans isomerization of the olefin provided that the lowest triplet state of the olefin was lower than that of the carbonyl compound. Photolytic studies by Cundall et al. (1964) have shown that isomerization of the 2-butenes can be effected using benzene or pyridine vapor as the sensitizer. Hammond et al. (1962) and Cundall et al. (1964) attributed their results to the transfer of energy from the triplet state of the sensitizer to the olefin, with the concomitant formation of the triplet state of the latter. Oxygen is also known to quench triplet states (Sester et al., 1962).

The rapid initial inhibition of the formation of about 70% of the 4-pentenal by oxygen or 1,3-pentadiene, followed by a much less efficient reduction of the remainder, suggests that two precursors of the aldehyde are involved. In view of the work of Hammond et al. (1962) and Cundall et al. (1964), and the above discussion of the feasibility of energy transfer, it is suggested that the lowest triplet state of cyclopentanone is responsible for about 70% of the 4-pentenal yield. The precursor of the remaining aldehyde has several possible identities, among which the present work does not distinguish. The lowest excited triplet state of cyclohexanone has been previously cited as the source of about 70% of the 5-hexenal from the radiolysis of cyclohexanone (Singh, 1963).

The quantity of material required by the analytical technique used necessitated irradiation of vapor phase samples at temperatures near the boiling point of cyclopentanone (131°C). The thermal instability of 4-pentenal mentioned previously (page 163), coupled with the susceptibility of the ketone to radiation induced oxidation, prevented the author from ascertaining any mechanistic differences between the formation of the aldehyde in the liquid and vapor phases.

The total radiolytic yield of the C_2 to C_4 products obtained from the vapor phase at 130°C (about 600 mm pressure) was four times greater than that formed from the liquid phase samples at 25°C (the total G values were 4.0 and 1.0, respectively). The difference in the amounts of ring fission may result from the difference in temperature, the lack of cage effect in the vapor phase, the formation of different excited states in the two phases, or a combination of these. Ramaradhya and Freeman (1961) found that the total yield of the C_2 to C_4 products from the radiolysis of cyclohexane was ten times larger for the vapor phase at 108° than for the liquid phase at 25°C.

b. Ethylene and Carbon Monoxide

The yields of carbon monoxide and ethylene are slightly sensitized by benzene and inhibited by pentadiene but their yields are not as strongly affected by either additive as is that of 4-pentenal. As mentioned above (see page 196 ff.) the states responsible for the formation of ethylene and carbon monoxide possess higher excitation energy than those which give rise to 4-pentenal. Since the average lifetime of excited states frequently decrease with increasing energy, the effects of additives on the deactivation or decomposition of a higher energy state should be less pronounced than those on a lower state. The effects of additives on the yields of ethylene, carbon monoxide, and 4-pentenal are therefore in line with expectations based on the relative energy requirements.

c. C_4 Products

Benzene appears to sensitize the formation of all of these products except perhaps n-butane (see Fig. III 12). This is to be expected in terms of the excitation energy of the excited states involved (see page 196 ff.). Oxygen completely inhibits the formation of n-butane, inhibits about one-half of the 1-butene, and exhibits little if any effect on the yields of methylcyclopropane and cyclobutane. The effects of oxygen on the yields of cyclobutane, 1-butene, and n-butane agree with those reported earlier by Bristowe

et al. (1964) who did not report methylcyclopropane as a product. The oxygen results can be explained largely in terms of radical scavenging reactions. Since the lifetime of a biradical is expected to be much shorter than that of a monoradical (Singh and Freeman, 1964c), oxygen would be expected to interfere with the formation of n-butane by scavenging the $C_4H_9\cdot$ radical formed in equation IV-44, but not with formation of the other C_4 products which arise from reactions IV-41 to IV-43. Once 1-butene is formed however, it may readily be attacked by RO_2 radicals as shown in equation IV-50 and IV-51.

$$R\cdot + O_2 \longrightarrow \dot{R}O_2 \qquad \text{(IV-50)}$$

$$\dot{R}O_2 + CH_2{=}CHCH_2CH_3 \longrightarrow RO_2{-}CH_2{-}\dot{C}HCH_2CH_3 \qquad \text{(IV-51)}$$

This explanation was suggested earlier by Bristowe et al. (1964).

5. A Comparison of Ring Fragmentation of Cyclopentanone with That of Cyclohexanone

An estimate of the radiation induced ring opening in cyclopentanone is given by equation IV-52.

$$G\text{ (ring opening)} \sim G_i\text{ (CO)} + G_i\text{ (4-pentenal)} = 0.68 + 0.84 = 1.52 \qquad \text{(IV-52)}$$

The accuracy of this approximation depends upon the mechanism of formation of 4-pentenal. If 4-pentenal is formed by an intramolecular hydrogen atom transfer involving

the tetramethylene acyl biradical, regeneration of a cyclopentanone molecule could occur by an intramolecular combination reaction. Thus, use of the observed yield of 4-pentenal would cause a low estimate to be made of the amount of ring opening.

A similar approximation of the amount of ring opening which occurs during the radiolysis of cyclohexanone gave a G value of 1.3 (Singh and Freeman, 1964a).

A comparison of these values with that obtained from the product yields of cyclohexane ($\sim$0.8)(Freeman, 1960) indicates that the cyclic ketones are somewhat less stable with respect to ring opening than alicyclic compounds due to the influence of the carbonyl group.

The data in Table IV 7 indicate that the fragmentation of cyclopentanone is slightly more extensive than that of cyclohexanone. The relative yields of the C_4 and C_5 compounds from the two ketones is probably due to the relative reactivities of the C_4 and C_5 biradicals. The tetramethylene biradical can decompose to form two molecules of ethylene and the activation energy of this reaction is only about 5 kcal/mole (Freeman, 1964). The pentamethylene biradical would produce one molecule of ethylene and a trimethylene biradical and this reaction would have an activation energy of about 22 kcal/mole (Singh, 1963). The much larger yield of ethylene from cyclopentanone (0.80) compared to that of

TABLE IV 7

Comparison of the Yields of the Fragmentation Products from Cyclopentanone and Cyclohexanone.

Cyclopentanone		Cyclohexanone[a]	
Product	G_i	G_i	Analogous Product
4-Pentenal	0.84	0.85	5-Hexenal
Carbon monoxide	0.68	0.48	Carbon monoxide
Total C_2-C_4	1.0	0.46	Total C_2-C_5
C_4 products	0.14	0.29	C_5 products

a: Singh (1963).

cyclohexanone (0.12) is therefore not surprising.

A further indication of the similarity between the reactivity of the two ketones is given by an estimate of the consumption of the ketones during radiolysis, which may be calculated by equation IV-53, e.g. for cyclopentanone:

$$\begin{aligned} G(\text{consumption of cyclopentanone}) &\sim G(CO) \\ &+ 2\,G(\text{cyclopentanol}) + 2\,G(\text{cyclopentenone}) \\ &+ G(\text{4-pentenal}) + 2\,G(\text{total dimer}) + G(\text{polymer}) \\ &= (0.68 \pm 0.06) + (1.68 \pm 0.30) + (0.18 \pm 0.08) \\ &+ (0.84 \pm 0.10) + (2.0 \pm 0.2) + (1.9 \pm 0.3) \\ &= 7.3 \pm 1.0 \end{aligned} \qquad \text{(IV-53)}$$

A similar calculation for cyclohexanone (Singh, 1963) gave a value of 7.3 ± 2.2.

6. Kinetic Considerations

It was concluded that reactions (16) and (17) occurred in the present systems.

$$M^* + S \longrightarrow M + S^* \qquad (16)$$

$$M^* \longrightarrow P \text{ (or } M) \qquad (17)$$

where M* was benzene or cyclopentanone in its lowest triplet state. Reaction (17) might involve more than one molecule or more than one step, but it is pseudo-first order. Values of k_{16}/k_{17} have been calculated from the results and are recorded in Table IV 8.

TABLE IV 8

The Ratio of the Rate Constant for Energy Transfer to that for First Order Decay.

M	S	k_{16}/k_{17}(l/mole)	Ref.
Cyclopentanone	oxygen	600	this work
Cyclopentanone	1,3-pentadiene	20	this work
Cyclohexanone	oxygen	2000	Singh and Freeman (1964c)
Cyclohexanone	2,3-dimethyl-1,3-butadiene	600	Singh and Freeman (1964c)
Benzene	cyclopentanone	2	this work
Benzene	cis-butene-2	30	Cundall and Griffiths (1963)
Benzene	trans-butene-2	17	Cundall and Griffiths (1963)
Toluene	benzoyl peroxide	450	Vasil'ev and Krongaus (1963)
2,5-Diphenyl-oxazole	benzoyl peroxide	40	Vasil'ev and Krongaus (1963)

If it is assumed that the oxygen quenching of the cyclopentanone species is a diffusion controlled reaction[2] with a rate constant of 10^{10} liters/mole sec, the lifetime of the species with respect to isomerization to 4-pentenal is about 10^{-7} sec. This is much shorter than the radiative lifetime of the lowest triplet state of cyclopentanone (estimated in the solid state at 77°K to be 1.1×10^{-3} sec by LaPaglia and Roquitte [1962]), so it is unlikely that there would be an observable amount of phosphorescence from liquid cyclopentanone.

Vasil'ev and Krongaus (1963) observed energy transfer from toluene to benzoyl peroxide during radiolysis or photolysis of dilute solutions of the latter in the former. During radiolysis they obtained G (excited molecules for energy transfer) = 8.5 and, considering the present work, it seems likely that the active species is the lowest triplet state of toluene. They obtained k_{16}/k_{17} = 450 liters/mole (cf. values for similar processes in Table IV 8).

Cundall and Griffiths (1963) studied the cis-trans isomerization of 2-butene in benzene solution, induced by gamma-rays. They observed G (cis $\longrightarrow$ trans) = 2.2 at concentrations of 2-butene greater than 0.2 M and suggested

---

2. Porter and West (1964) found that oxygen had a collision efficiency of about 7×10^{-3} for quenching triplet states of naphthalene and anthracene in the gas phase. In the liquid phase there would be a great many collisions per encounter between the oxygen and the triplet species. Thus the above assumption is not unreasonable for an order of magnitude calculation.

that the mechanism involved energy transfer from the lowest triplet state of benzene molecules. A value of k_{16}/k_{17} $\approx$ 30 liters/mole can be derived from their result.

The ratio k_{16}/k_{17} may be considered to be an energy transfer efficiency ratio and, as expected, it depends greatly upon the species involved in the transfer reaction (see Table IV 8).

C. Summary

The formation of products arising from C-C bond cleavage can readily be explained in terms of a biradical mechanism but a concerted process cannot be ruled out. Benzene appears to affect the yields of all products by participating in activation transfer reactions.

1,3-Pentadiene inhibits the yields of all major products either by activation transfer or radical scavenging reactions.

There are a great many similarities between the radiolytic decompositions of cyclopentanone and cyclohexanone.

Future work which might resolve the biradical vs. concerted process controversy could involve the radiolysis of a substituted cyclopentanone molecule possessing an optically active alpha carbon. Evidence of racemization of the recovered ketone would indicate a biradical path for decomposition. Such a reaction would require, however, that the lifetime of the biradical be sufficient to permit rotation of the group to occur.

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APPENDIX

An Additional Scavenging-Type Mechanism

Mechanism 4.

$$C_5H_8O \xrightarrow{I_4} C_5H_8O^+ + e^- \qquad (18)$$

$$C_5H_8O^+ + C_5H_8O \longrightarrow C_5H_8OH^+ + (C_5H_7O)\cdot \qquad (19)$$

$$C_5H_8OH^+ + e^- \longrightarrow (C^*) \longrightarrow H_2 + \text{residue} \qquad (20)$$

$$C_5H_8O^+ + In \longrightarrow C_5H_8O + In^+ \qquad (21)$$

$$In^+ + e^- \longrightarrow In^* \qquad (22)$$

$$In^* \longrightarrow (C^*) \longrightarrow H_2 + \text{residue} \qquad (23)$$

$$In^* \longrightarrow In \qquad (24)$$

Steady state treatment of this mechanism gives the following expression.

$$\left[1 + y(MR)\right]\rho = 1 + z(MR)$$

$$\text{where } y = \frac{k_{21}k_{23}}{k_{19}(k_{23} + k_{24})}$$

$$\text{and } z = \frac{k_{21}}{k_{19}}$$

and the other symbols have meanings similar to those given for Mechanisms 1 and 2.

An Additional Activation Transfer Type Mechanism

Mechanism 5.

$$C_5H_8O \xrightarrow{I_5} (C_5H_8O^+ + e^-) \qquad (25)$$

$$(C_5H_8O^+ + e^-) \longrightarrow (C^*) \longrightarrow H_2 + \text{residue} \qquad (26)$$

$$(C_5H_8O^+ + e^-) + In \longrightarrow (C_5H_8O^+ + In^-) \qquad (27)$$

$$(C_5H_8O^+ + In^-) \longrightarrow (C^*) \longrightarrow H_2 + \text{residue} \qquad (28)$$

$$(C_5H_8O^+ + In^-) \longrightarrow C_5H_8O + In \qquad (29)$$

where $(C_5H_8O^+ + e^-)$ is used to indicate that the electron does not escape the influence of the parent ion and is therefore not an independent entity.

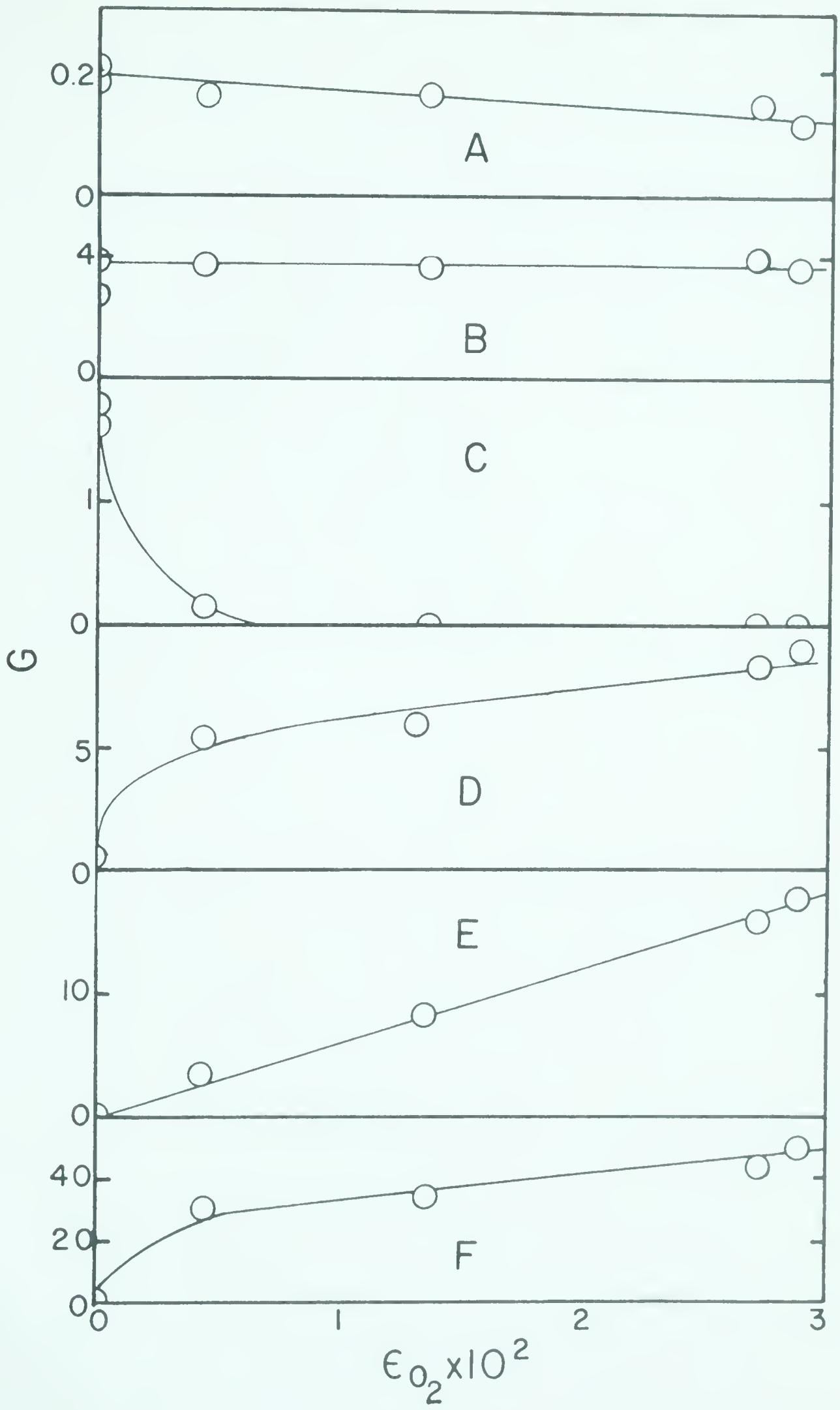
Steady state treatment leads to the following expression:

$$(1 + v[In])\rho = 1 + u[In]$$

where $$v = \frac{k_{27}k_{28}}{k_{26}(k_{28} + k_{29})}$$

$$u = \frac{k_{27}}{k_{26}}$$

and the other symbols have meanings similar to those given for Mechanisms 1 and 2.


0.2
A
0
4
B
0
C
1
0
G
5
D
0
E
10
0
40
20
F
0
0
1
2
3
$\epsilon_{O_2} \times 10^2$